

CHALCOGEN DOPANTS IN SILICON ELECTRONIC DEVICES

by

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This thesis is a study of the electronic properties of the chalcogens S, Se and Te as dopants in silicon and how these, in the case of Se, affect the characteristics of electronic devices. Special emphasis has been placed on the properties of npn transistors manufactured using IC technology. The work is presented in the following papers.

- I Capture processes at double donors in silicon
Phys. Rev. B 31, 3659 (1985)

- II Recombination and generation processes in selenium-doped silicon
Manuscript

- III Properties of selenium-doped silicon npn transistors
Manuscript (accepted for publication in Solid-State Electron.)

- IV Anomalous phosphorus and boron diffusion in selenium-implanted npn silicon transistors
Manuscript

- V Switching properties of selenium-doped silicon npn transistors
Manuscript

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The summary of this thesis is divided into the following sections:

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INTRODUCTION

In the development of solid-state electronics, considerable scientific effort has been devoted to studies of the impurity and defect centres in semiconductors. The decisive role of point defects in semiconductors was a driving force behind the investigation of both their experimental and theoretical aspects. Such a physical property of semiconductors as the electrical conductivity can be modulated by several orders of magnitude by doping with impurities. The material can be chosen to be either n- or p-type by introducing donor or acceptor levels, respectively. The possibility of simultaneous doping of a semiconductor with different impurities resulted in the development of electronic devices such as transistors. The invention of the transistor caused a major revolution in the technology and information processing of our society.

The development of electronics is taking two different paths. One is the higher integration of the integrated circuits (IC's), resulting in smaller dimensions and higher speed, the other is

heading towards more power and higher voltage capability. Both of these branches require more basic research on impurity and defect centres, since other than desirable effects result from their presence in semiconductors. Deep-level defects may have a deleterious influence on the performance of electronic devices, such as increased noise and leakage current in diodes and transistors. Furthermore, a decreased current gain in transistors and reduced output of solar cells due to enhanced recombination etc. may be related to deep-level defects.

However, deep-level defects can occasionally be introduced into electronic devices in order to improve some of their properties. This is the case with switching power devices, where the excess charge carriers with finite lifetimes are responsible for switching delays and power losses. Since the deep-level impurities have a profound effect on the semiconductor lifetime, they can be used to control switching properties of the devices. Gold and later platinum have been used for a long time for this purpose. These species create deep acceptor and donor levels in the band gap of a silicon crystal^{1,2}. The acceptors act as recombination centres in n-type silicon and the donors do the same in p-type silicon. One drawback, especially in the case of gold, is the increased leakage current. Recently, electron irradiation has become popular for the creation of deep-level defects in silicon power devices.

However, none of these methods could be easily performed for selective lifetime control on integrated circuits for power applications.



During recent years some interest has been paid to the chalcogen impurities in silicon. Chalcogens, especially Se, have already been used for doping III-V semiconductors. In GaAs for example group VI elements on As sites give rise to shallow donors. In silicon, the chalcogens S, Se and Te create deep levels.

S and Se doping in Si has found some application in IR-detectors³⁻⁵. These detectors are used for the 3-5 μm IR-band. No other applications of chalcogen-doped silicon devices have, to the best of the author's knowledge, been discussed in the literature.

However, it was recently suggested that at least S and Se could act as recombination centres due to the very large electron-capture cross-sections exhibited by the levels created by them^{6,7}. Since no results on hole-capture cross-sections were published at that time, it was impossible to establish if this assumption was true. This lack of detailed knowledge of the hole capture processes of chalcogen-doped Si was one of the essential motives for the work presented in this thesis. Another is the possibility of selective doping with deep-level impurities, acting as recombination centres, by means of ion implantation. Such a feature could open up new possibilities in the design of electronic devices.

Silicon and chalcogens, S, Se and Te

Crystalline silicon has a diamond structure with a lattice constant of 0.357 nm. The bonds are covalent with a binding energy of 1.8 eV. These bonds are the sp^3 hybrid orbitals giving a

tetrahedral-symmetry configuration. A perfect Si crystal has a band structure with an indirect forbidden band gap as shown in Fig. 1.

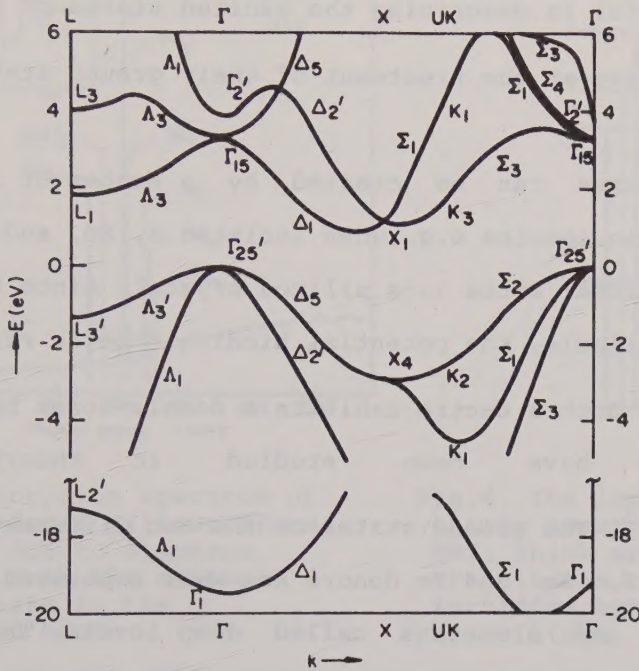


Fig.1. The energy band structure of Si (from Ref. 8)

When an impurity atom replaces an atom of the host silicon lattice, the potential of the impurity may give rise to electronic states in the forbidden energy band gap. These impurity centres are usually divided into so-called shallow and deep levels, depending on the energy position of the ground state.

The donor states, produced by the atoms belonging to the fifth group in the periodic table, have a ground-state energy of the order of 50 meV and are called shallow, for historical reasons. The potential binding the extra electron to the donor is often approximated by a hydrogen-like potential, adjusted by the

dielectric constant and the effective mass of the charge carrier. The energy levels created by such a potential are satisfactorily described by the effective-mass theory (EMT) (or Kohn-Luttinger effective mass theory after its founders)⁹⁻¹¹. The EMT formalism can also be useful in describing the excited states of some deep centres¹², but fails at the treatment of their ground states.

Deep-level centres can be created by a number of intrinsic defects or atomic species e.g. when isolated S, Se, and Te atoms occupy substitutional sites in a silicon crystal. Since two extra electrons are available, the potential binding them is referred to as helium-like¹³. Such a centre exhibits a double-donor behaviour. Double donors have been studied in theory quite extensively^{8,13-15}. The ground states of the two different charged states of the S, Se and Te donors are well separated from the conduction band and are thus called deep levels. The binding energies are shown in Fig. 2. In addition, the series of excited states is present in the band gap. Fig. 3 shows the absorption spectrum of selenium-doped silicon. The lines in this spectrum correspond to the allowed transitions in a surrounding with a tetrahedral symmetry, shown in Fig. 4.

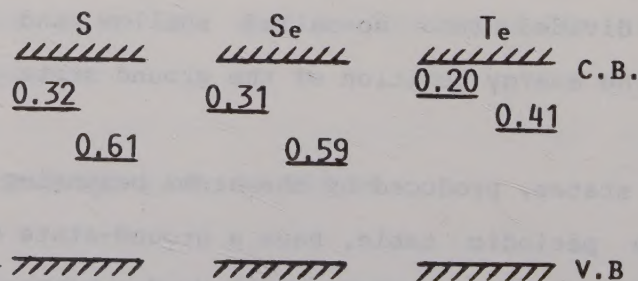


Fig.2 The binding energies of the chalcogenide isolated double donors in silicon (from Refs. 12 and 16).

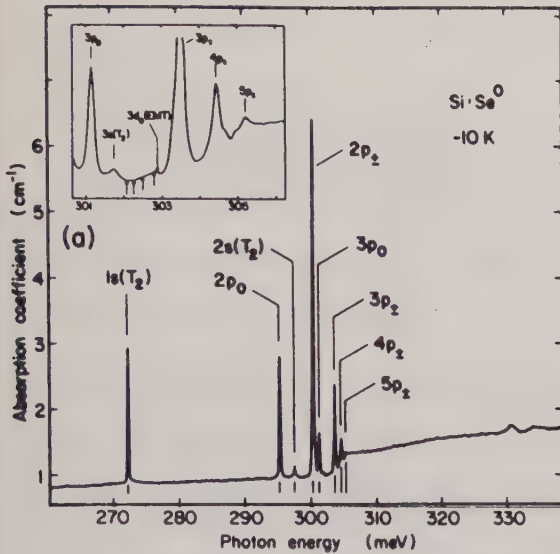


Fig.3. Absorption spectrum of selenium-doped silicon (from Ref. 16) due to electron emission from the neutral charge state to the conduction band.

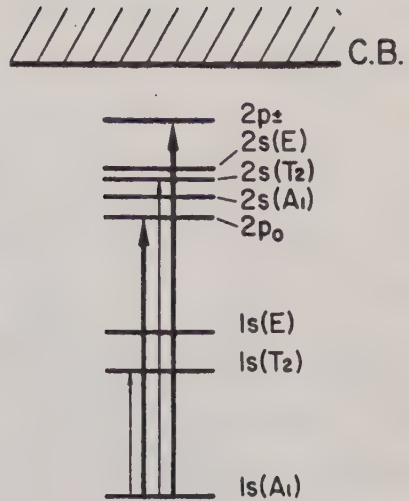


Fig.4. The lower part of the energy spectrum according to EMT. Thick arrows: EMT-allowed transitions, thin arrows: EMT-forbidden but symmetry-allowed transitions.

Since the isolated chalcogen donors (S, Se and Te) give rise to two dominant levels in the band gap, they have been investigated extensively. The electron capture has been studied for the S and Se two-electron levels^{6,7} (the singly ionized state). The electron capture to the one-electron levels (the doubly ionized states) and both Te levels were too fast to be measured. The electron-capture cross-sections for two-electron S and Se levels showed a temperature dependence of $T^{-3.3}$ and $T^{-3.2}$, respectively, indicating a cascade process in agreement with Abakumov's theory¹⁷.

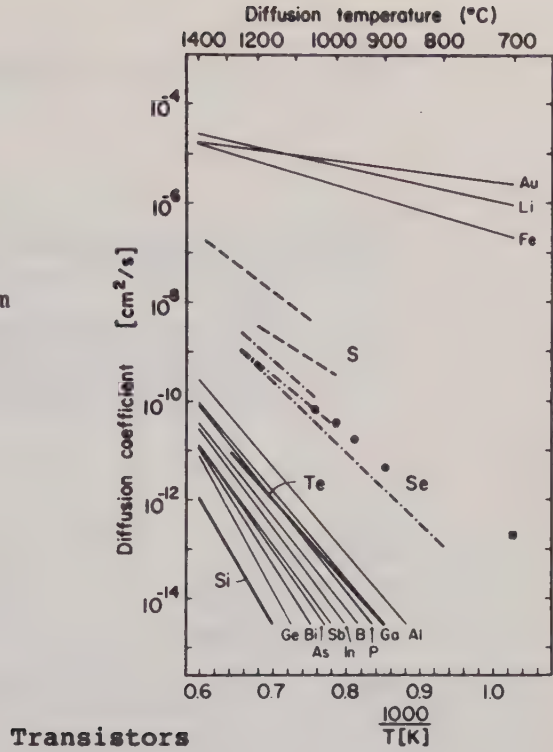
The hole capture to the S, Se and Te centres has been studied in paper I of this thesis. The hole capture to the two-electron

levels (the neutral states) proved to be an Auger process. The Auger capture at double donors has been treated in theory rather extensively^{18,19} but few such processes have been studied experimentally.

S and Se give rise to other levels in the silicon bandgap than those created by the isolated double donors. High resolution studies of S- and Se-related donor centres in silicon were performed by Janzen et al.¹⁶ In addition to the isolated double donors, complexes, such as pairs, may be identified. The pair formation was found to depend on the conditions prevailing during the doping process.

The diffusivities of S, Se and Te have been investigated²⁰⁻²⁶ and to be found dependent on the atom size. S and Se are much faster diffusants than tri- and pentavalent dopants, while Te diffuses at rates similar to those of phosphorus. A comparison with diffusion rates of other impurities in silicon is shown in Fig. 5. Since there is no generally valid model of diffusion in silicon no explanation to the mechanisms of the chalcogen diffusion in silicon has been given. A suggestion was made by Janzen et al.²⁰ that Te diffusion is mainly substitutional while S and Se diffuse interstitially in greater proportions.

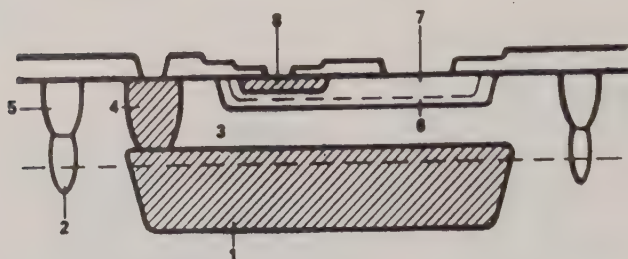
Fig.5.
The diffusion coefficients of chalcogenide dopants in silicon in comparison with commonly used dopants (from Ref. 20).



Since one purpose of this work was to study the effects of selective doping of integrated circuits with lifetime-controlling impurities, the devices studied in this thesis were npn transistors incorporated into IC's. The IC's were produced with a high-voltage bipolar process, developed by the author²⁷. A schematic picture of such a transistor is shown in Fig. 6.

The history of the transistor began in 1947 at Bell Laboratories, USA. In 1948 J. Bardeen and W. Brattain described a point-contact transistor²⁸. The following year W. Shockley published the basic paper on the small-signal theory of the transistor²⁹. The theory was extended by the Ebers-Moll model³⁰ which related physical device parameters to device terminal

NPN-Transistor with plug and iso-up



- | | | | |
|----|-------------------|----|-----------------|
| 1. | BURIED LAYER | 5. | ISOLATION |
| 2. | ISOLATION IMPLANT | 6. | LOW DOPED BASE |
| 3. | EPITAXIAL LAYER | 7. | HIGH DOPED BASE |
| 4. | PLUG | 8. | EMITTER |

Fig. 6. Cross-section of the transistor used in the experiments.

characteristics. Further improvements to the large-signal analysis of the switching transistor were made by introducing the concept of the transistor as a charge-controlled device^{31,32}.

The central point in the charge-controlled transistor model is the obvious relationship

$$dI = \frac{dQ}{t}$$

where t is a time constant relating the current to the charge.

The Gummel-Poon model³², which is the most widely used today, links junction voltages (see Fig. 7), collector current and base charge

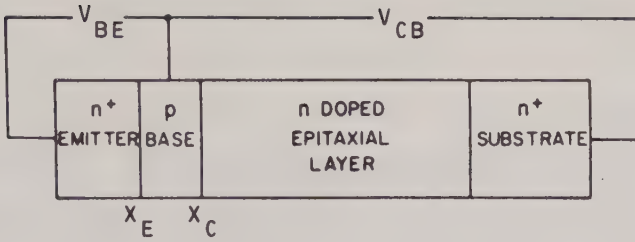


Fig. 7. npn transistor with bias voltages.

in one equation

$$I_{CC} = AJ_{CC} = (qn_i A)^2 D_B \frac{\exp(qV_{BE}/kT) - \exp(qV_{BC}/kT)}{qA \int_0^w n(x) dx}$$

where J_{CC} is the collector current of an ideal transistor with unity gain and A is the transistor area.

The device modelling reduces to modelling the base charge

$$Q_B = qA \int_{x_E}^{x_C} n(x) dx$$

which consists of five components

$$Q_B = Q_{B0} + Q_{jE} + Q_{jC} + Q_{dE} + Q_{dC}$$

where Q_{B0} is the base charge at zero bias, Q_{jE} and Q_{jC} are charges associated with emitter and collector depletion-region

capacitances, respectively, Q_{dE} and Q_{dC} are minority excess charges associated with emitter and collector diffusion capacitances. The diffusion capacitances increase with increasing injection level.

The switching speed of a transistor depends on the time constants related to the different charges. For an epitaxial transistor the excess charge injected into the collector can limit the switching time. Impurities like gold were used to enhance the recombination in the collector and base regions, thus speeding up the transistors in TTL circuits. However, an increased leakage current was a highly undesirable side-effect. Further, modern circuits include a number of other devices e.g. lateral pnp transistors, which can not function with gold doping, and unfortunately, gold doping can not be performed selectively due to its very high diffusivity.

An improvement was made by introducing Schottky clamp diodes. These diodes are connected in parallel to the base-collector diodes of the transistors. Since the forward voltage drop for a Schottky diode is lower than for a pn diode, the charge carrier injection is reduced considerably. An obvious result is a decreased switching time. It is not practical to use Schottky clamps in high-current applications due to rather high series resistances. For high currents, this leads to an increased voltage drop between collector and base terminals and increased injection of minority carriers.

The injection of minority carriers into the epitaxial collector results in further problems. An npn transistor incorporated in an

IC is in reality a four-terminal device, where the fourth terminal is the substrate, as shown in Fig. 8. This results not only in the desirable, active transistor but also in a parasitic pnp transistor with the substrate as the collector. The base and collector of the npn transistor form the emitter and the base of the parasitic pnp transistor, respectively. Such a parasitic pnp action can be deleterious for an IC's performance. Several ways to minimize this problem have been applied e.g. guard rings, extra p-collectors to pick up the minority holes or circuits to eliminate saturation. Another way to solve the problem could be to decrease the current gain of the parasitic transistor by killing the lifetime selectively in the epitaxial layer. Even if it was not shown in this thesis, chalcogens could be applied for this purpose.

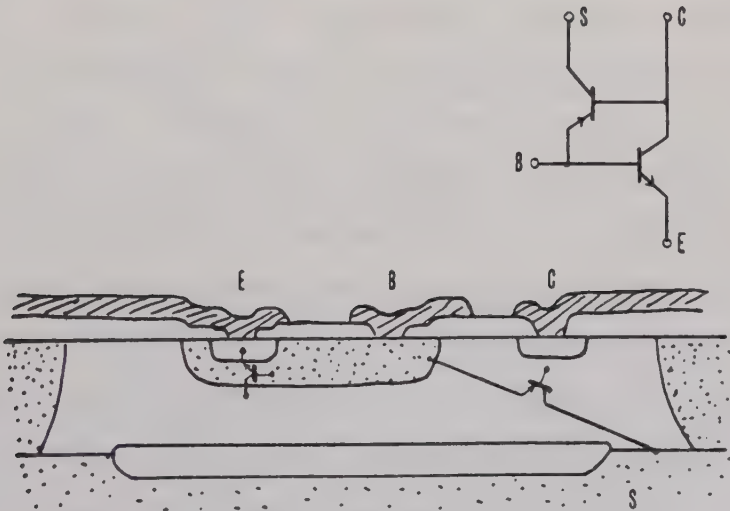


Fig. 7. Parasitic pnp transistor associated with an npn transistor in an integrated circuit.

Experimental techniques

This thesis contains the results of several investigations of the basic properties of the chalcogen defects in Si, as well as of the device properties caused by the incorporation of these defects in the device structure. Thus, a number of different analytic techniques have been used:

- Junction space-charge techniques, both steady state and transient
- Spreading Resistance Probe technique (SRP)
- Secondary Ion Mass Spectroscopy (SIMS)
- Various electrical parameter measurement techniques for device characterization.

Junction space-charge techniques are reviewed in Refs. 33,34. These techniques enable studies of both thermal and optical emission and capture processes at impurity levels in the bandgap as well as the concentration of the defects. This is generally achieved by affecting the occupancy of the levels in the depletion region of a diode by an external disturbance of e.g. light, temperature, electric pulse etc. The change in the level occupancy manifests itself as a change in the capacitance or current. An elegant and very convenient transient space-charge technique is Deep-Level Transient Spectroscopy (DLTS), originally suggested by Lang³⁵. DLTS techniques have become almost the standard industrial technique for the characterization of semiconductor defects.

The Spreading Resistance Probe technique^{36,37} is a widely used method for measuring the free carrier concentration in

semiconductor devices. This concentration is a function, in the case of an extrinsic semiconductor, of the concentration of the electrically active impurities. Basically, SRP is performed by angle-lapping a sample and measuring the two-point spreading resistance of the lapped surface. From SRP data the charge carrier concentration is computed. The charge carriers' profiles reveal the net impurity concentrations and the positions of all pn junctions, thus characterizing an electronic device. The technique is very straightforward though it is very sensitive to the calibration.

A supplementary technique is Secondary Ion Mass Spectroscopy³⁸. This method makes it possible to evaluate the chemical identity and concentration of the impurities. In a SIMS measurement the successive atom layers are sputtered off from the surface of a sample by an ion beam. The secondary ions, coming from the surface, are analysed in a mass spectrometer. Since the sputter rate is known, the concentration of different species in the sample can be determined as a function of depth.

The combination of SIMS and SRP provides a powerful tool for the analysis of the electrically active and chemical impurity distributions in semiconductors. This knowledge is crucial for the understanding of the properties of electronic devices.

The above-described methods give information about basic properties of the impurities and their distribution in the electronic devices. To evaluate the effects of their presence, a number of static and pulsed I-V techniques must be employed to

characterize the devices. Thus, forward and reverse I-V diode characteristics, current gain for the transistors, breakdown voltages, turn-on and -off delay times etc., define the operating region for the measured devices. These parameters are usually extremely sensitive to all changes in the device structure and composition. Using well-developed device-physics theory it is possible to connect properties of the impurities with the device properties.

Summary of the papers

This thesis had as a goal the study of recombination properties of the chalcogens S, Se and Te in silicon devices. The first step was the investigation of hole-capture processes at chalcogen double donors (paper I). Subsequent work (papers II-V) concentrated on the effects of selenium doping. The results showed that Se forms efficient recombination centres in Si. Electronic devices with complex structures, such as transistors incorporated in IC's, were Se-doped. These transistors, although affected by Se doping, were operative devices exhibiting some interesting properties, such as high switching speeds and low reverse-bias currents. A more detailed summary of the presented work follows.

I Capture processes at double donors in silicon

In this paper the hole-capture processes at isolated, substitutional, chalcogen double donors in silicon have been studied. Various steady-state and transient-capacitance

measurement techniques were employed. Absolute values of hole-capture cross-sections were obtained for capture to both neutral, D^0 , and singly ionized, D^+ , S, Se and Te donors.

The results were best interpreted as multiphonon emission (MPE) and radiative capture processes for the S^+ centre, radiative for the Se^+ and Te^+ centres and an Auger process for S^0 , Se^0 and Te^0 centres. The Auger capture process at He-like centres is especially interesting, since this has been discussed in theory but very few cases have been studied experimentally.

It was also unambiguously shown that the D^0 and D^+ energy levels correspond to the neutral and singly ionized versions of the double donor, respectively.

II Recombination and generation processes in selenium-doped

silicon

The results of paper I and previous work⁷ are combined in order to discuss recombination and generation properties of Se double donors in silicon devices.

Using multiple-level recombination statistics, the lifetimes of the excess charge carriers are calculated. It is shown that the Se double donor is most efficient as a recombination centre in n-type silicon since the two-electron level is mainly responsible for the recombination.

An improved diode-preparation technique resulted in heavily selenium-doped diodes with a very low reverse dark current. This

current was comparable to the reverse-current of the reference devices. The results of the thermally-stimulated current measurements showed that previously published data on hole-emission rates from doubly ionized Se donors must be at least one order of magnitude too high and that the emission rate is probably much less than 10^{-1}s^{-1} at room temperature. The conclusion drawn was that the Se double donors act as recombination centres but are very inefficient generation centres.

III Properties of selenium-doped silicon npn transistors

The study of selenium centres in papers I and II resulted in an effort to manufacture some electronic devices of higher complexity and to study the influence of selenium on their properties. Silicon npn transistors were prepared using IC technology, and were then selectively ion-implanted with selenium.

The steady-state characteristics of the transistors were studied using standard measurement techniques. The results showed that the collector saturation current decreased, and base current increased, with implanted selenium dose. The reverse dark current was not affected. Additional material investigations showed that the dopant profile was heavily influenced by selenium implantation.

The changes in transistor characteristics are discussed in terms of the results of observed dopant redistribution and increased recombination in n-type emitter and collector.

IV Anomalous P and B diffusion in selenium-implanted npn silicon transistors

This work is an extension of paper III. SIMS and SRP measurement techniques were employed to investigate the impurity redistribution in selenium-implanted transistors. The measurements showed that both phosphorus and boron profiles were affected by selenium ion implantation. The phosphorus-emitter profile became shallower while the base profile showed an increased boron concentration.

The emitter diffusion retardation was interpreted as a result of implantation-induced disorder-stress which, as it has previously been shown in the literature, decreased the diffusivity of phosphorus in silicon.

The cooperative diffusion effects were suggested as a reason for the boron diffusion enhancement.

V Switching properties of selenium-doped npn silicon transistors

The results of papers II and III and the basic transistor-operation theory suggested improved switching properties of the selenium-doped transistors. Using a standard pulse-measurement technique the turn-off delay time for the transistors was investigated. As expected, the delay time decreased with increasing selenium dose. The trend in this decrease is compared with theory.

Acknowledgments

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Capture processes at double donors in silicon

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The hole-capture processes at isolated double donors in chalcogen-doped silicon have been investigated. Different steady-state and transient-capacitance techniques were used. It is shown that the capture process at neutral centers is governed by an Auger-type capture process at a He-like center. The hole-capture cross sections for neutral centers are almost temperature independent and have values of about 10^{-16} cm². The processes for hole capture at singly ionized centers are best described as a multiphonon emission and/or a radiative process. At low temperatures the cross sections are about 10^{-24} – 10^{-22} cm².

I. INTRODUCTION

Good insight into the recombination processes of free charge carriers has long been considered important in both applied and basic research. The free-carrier lifetime controls the properties of most semiconductor devices, and recombination processes are frequently used to study important parameters of semiconducting materials. Recombination is often discussed in terms of radiation, cascade, multiphonon-emission, or Auger processes. The particles involved are photons, phonons, or other charge carriers.¹ In moderately doped semiconductors with indirect band gaps the lifetime of free charge carriers is generally determined by recombination via energy levels in the forbidden energy gap. These energy levels may be due to either shallow or deep centers originating from both intrinsic and extrinsic defects. The defects known as EL2 in GaAs and gold in silicon are typical examples of lifetime-controlling defects in semiconductors.

The capture of electrons into the singly charged isolated sulfur and selenium centers in silicon has recently been studied in some detail.^{2,3} It has been shown that electron capture into these centers is probably governed by a cascade or at least a two-stage capture process via excited states. The capture cross sections describing the electron capture into the doubly ionized sulfur and selenium centers in silicon have been found to be very large and hitherto no absolute values of these cross sections have been reported.

The purpose of this paper is to report on the capture of holes at the isolated sulfur, selenium, and tellurium centers in silicon. Reviews of these centers are given in Refs. 4–6. In this paper it is shown unambiguously that these centers are indeed double donors. The temperature dependence of the hole-capture cross section has been studied for both neutral and singly positively charged centers. However, a major part of our study has been de-

voted to the hole capture of neutral centers showing that this process is governed by an Auger-type capture process.

II. HOLE CAPTURE AT NEUTRAL AND REPULSIVE CENTERS

A double donor has three charge states: a neutral, a singly positively charged, and a doubly positively charged state. The three charge states will be denoted D^0 , D^+ , and D^{2+} , respectively. In the neutral state two electrons are bound to the double donor. There are two ways of changing the charge state of the center from a neutral to a singly charged state: either by exciting an electron from the center into the conduction band or by capturing a hole from the valence band as described by the following equations:

$$D^0 \rightarrow D^+ + e \text{ for electron emission,} \quad (1)$$

$$D^0 + h \rightarrow D^+ \text{ for hole capture.} \quad (2)$$

There is, however, a fundamental difference between these two processes. In the first case, electron emission, the center absorbs energy, whereas in the second case energy is released. The released energy must be carried away and may trigger other processes. If the hole capture is radiative and reabsorption of the emission is not important, the capture process, as described in Eq. (2), will result in a singly positively charged center. If, however, the hole capture is nonradiative and the released energy is carried away by another particle or particles a different final charge state may result. For example, the neutral chalcogen centers are located in the upper half of the band gap [Fig. 1(a)] and enough energy is released during the hole-capture process to excite the second electron of the double donors into the conduction band. The equation describing such a process is

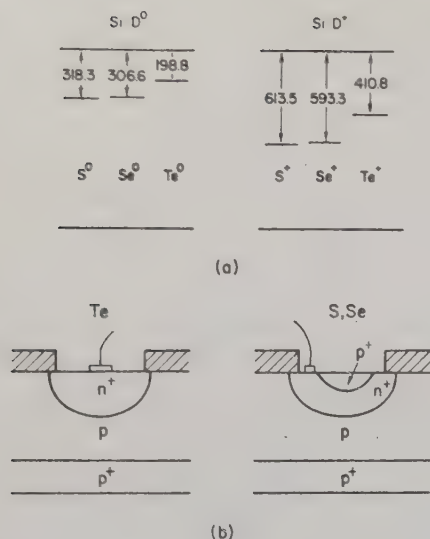


FIG. 1. (a) Optical binding energies for isolated D^0 and D^+ centers in chalcogen-doped Si (from Refs. 4 and 6). (b) n^+p and p^+n^+p sample structures used in this work.



and the process is known as an Auger-type capture process for a He-like center. The final charge state is, therefore, in this case, a doubly positively charged center.

This type of Auger capture has been suggested previously as a possible mechanism for the capture of free charge carriers into deep centers, but to the best of our knowledge it has never been studied experimentally. Theoretical considerations⁷⁻¹⁰ show that the Auger-type capture process should result in weakly-temperature-dependent capture cross sections in the range 10^{-20} – 10^{-14} cm², in agreement with our results.

The D^+ centers are singly positively charged and therefore repulsive to holes. Hole capture at these centers is therefore best described by different types of processes such as radiative capture processes and/or multiphonon-emission (MPE) processes. Our data indicate that different hole-capture processes may occur at singly charged sulfur, selenium, and tellurium donor centers in silicon.

III. EXPERIMENTAL DETAILS

The samples used in this paper were either n^+p diodes or n^+p diodes in p^+n^+p transistor structures employing a 1.5×10^{15} cm⁻³ boron-doped epitaxial layer as the p region [Fig. 1(b)]. The n^+p and p^+n^+p structures were doped with chalcogens by ion implantation as the dopant source and, as in the case of Se, solid-state diffusion. In all cases the implantation depth was less than 2000 Å, i.e., much smaller than the depth of the n^+ region. The n^+p structures were used for diffused Se and implanted Te samples. In the case of Te the n^+ diffusion was done after in-diffusion of the implanted Te due to the high temperature needed for the latter process.

Varying implantation procedures were employed for different chalcogens. In the case of sulfur, a dose of 5×10^{14} cm⁻² at 60 keV was used for implantation of a p^+n^+p transistor structure. After deposition of a 4000-Å-thick SiO₂ layer on top of the sample in a chemical-vapor-deposition (CVD) reactor at 420°C, the diode was diffused in an open-tube furnace for 1 h at 1000°C in a nitrogen atmosphere. Contact holes were then opened in the SiO₂ layer by means of a photolithographic process, and an aluminum layer was sputtered onto the surface, forming an Ohmic contact. The electrically active sulfur concentration (D^0 and D^+) was typically 4×10^{12} cm⁻³, which was about 0.4% of the shallow-level concentration as deduced from deep-level transient-spectroscopy (DLTS) measurements. The net shallow-level concentration in the p region was 1×10^{15} cm⁻³.

Selenium doping was performed at a dose of 10^{14} cm⁻² at 100 keV. After diffusion in an oxygen atmosphere for 1 h at 900°C, a selenium (Se⁰ and Se⁺) concentration of about 7% (5×10^{13} cm⁻³) of the shallow-level concentration in the p region was generally detected. The net shallow-level concentration was found to be 7×10^{14} cm⁻³. Se-doped samples were also made using a solid-state diffusion procedure. A small amount of Se together with some n^+p diodes and Si powder were put in a quartz ampoule. After evacuation, the sealed ampoule was put into an open furnace for 1 h at 930°C. The shallow-level concentration was about the same in both implanted and diffused samples. The Se⁰ and Se⁺ concentration was about 9% (6×10^{13} cm⁻³) of the shallow-level concentration in the p region.

Tellurium doping was achieved by ion implantation into a p -type epitaxial layer using a dose of 10^{13} cm⁻² at 100 keV. The samples were then diffused in an open furnace at 1250°C for 15 min in an oxygen atmosphere. In order to avoid overly thick oxide layers the diffusion continued for 45 min in a nitrogen atmosphere. The n^+p junction, 1.5 μm deep, was formed by phosphorous deposition at 920°C for 20 min and diffusion in an oxygen atmosphere at 1000°C for 30 min. The Te⁰ and Te⁺ concentration obtained using this procedure was typically 9% (6×10^{13} cm⁻³) of the shallow-level concentration. The net shallow-level concentration in the p region was 7×10^{14} cm⁻³.

Junction-space-charge techniques are particularly suitable for investigations such as the ones described in this paper since they allow for a distinction between minority- and majority-charge-carrier-transfer processes. Various forms of junction-space-charge techniques were therefore employed in our investigations, including both transient and steady-state methods.¹¹ Emission rates were measured using deep-level transient spectroscopy¹² and single-shot capacitance techniques, while capture rates were studied using both DLTS techniques and pulse-train methods.³ The free-hole concentration was, in all cases, determined from C^{-2} - V plots.

IV. EXPERIMENTAL RESULTS

To make sure that the chalcogen-related centers studied in our ion-implanted samples are indeed the same centers

as investigated previously in diffused samples, the thermal emission rate of electrons was measured for both the D^0 and D^+ centers in our sulfur-, selenium-, and tellurium-doped samples. Comparing our results (Fig. 2) with those previously published^{2,3,13} on chalcogen-doped silicon, it is quite evident that the same centers are formed in ion-implanted samples as in diffused samples.

The capture rates for holes were measured in n^+p diodes by first occupying the D^0 and D^+ centers with electrons using a minority-carrier-filling pulse and then monitoring the decrease in the capacitance due to a majority-carrier pulse train of constant pulse length. The measurements were first performed on the D^+ centers after thermal excitation of the first electron of the D^0 centers. The hole-capture cross section σ_p was then calculated from the hole-capture rate $\sigma_p v_{th} p$; where v_{th} is the thermal velocity and p is the hole concentration. v_{th} is defined by

$$v_{th} = (3k_B T / m_p^*)^{1/2},$$

where k_B is the Boltzmann constant, T is the temperature, and $m_p^* = 0.70 m_e$ is the effective mass of the holes. The hole-capture cross sections calculated from the measured capture rates are presented in Fig. 3. At low temperatures the cross sections for the capture of holes into the singly positively charged chalcogen centers are of the order of 10^{-24} – 10^{-22} cm². The largest cross section was found for the S^+ center and the smallest value was measured for the Te^+ center. Whereas the cross section for the S^+ center showed a pronounced temperature dependence, the hole capture into the Se^+ and Te^+ centers was almost independent of temperature in the temperature region studied. In order to increase the temperature region for the sulfur-doped samples, similar measurements were performed using DLTS.

Investigations performed on neutral chalcogen centers

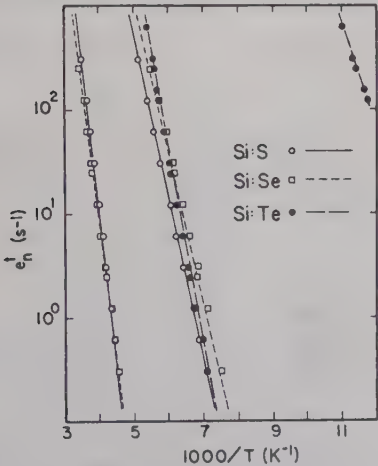


FIG. 2. Comparison of thermal emission rates of electrons obtained in implanted samples (this work) and diffused samples (from Refs. 2, 3, and 13) (straight lines). The straight lines for thermal Se and Te have been extrapolated.

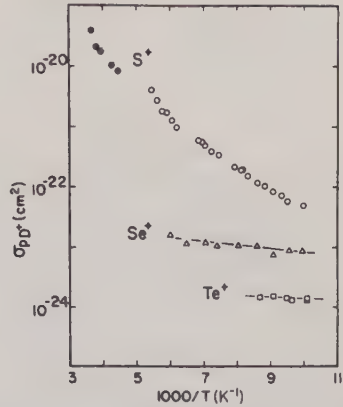


FIG. 3. Hole-capture cross sections for D^+ centers deduced from pulse-train and DLTS (solid circles) measurements.

gave values for the hole-capture cross sections in the region 10^{-17} – 10^{-16} cm² for all three chalcogens (Fig. 4). The largest capture cross section was again obtained for the sulfur center, while the smallest cross section was measured for the tellurium center. In all three cases only a weak temperature dependence was observed. Since the capture cross sections of holes for the D^+ centers were at least 3 orders of magnitude smaller than those for the D^0 centers, the hole capture into the D^0 centers could readily be measured without any disturbance from the D^+ centers. Owing to the small S concentration in the n^+p diodes, it was not possible to measure $\sigma_p D^0$ using the pulse-train method.

The pulse-train method gave, in all cases, a single-exponential dependence of the diode capacitance on the number of pulses. To demonstrate this, the time dependence of the capacitance due to the capture of holes into the Se^0 and Se^+ centers is shown in Fig. 5 for a measure-

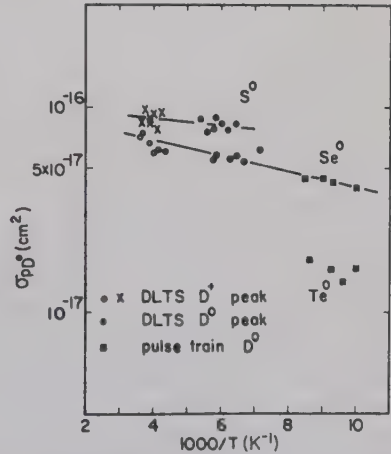


FIG. 4. Hole-capture cross sections for D^0 centers. Three different measurement techniques have been used: pulse train, DLTS on the D^0 peak, and DLTS on the D^+ peak. See text for details.

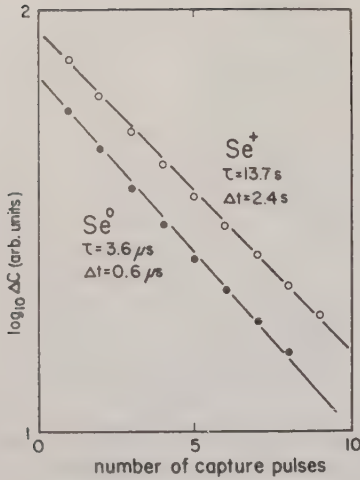


FIG. 5. Transients obtained from the pulse-train technique for the Se^0 and Se^+ centers at about 120 K. The transients are single exponential and the time constants differ by about 7 orders of magnitude. Δt is the constant majority-carrier pulse length.

ment performed at about 120 K. In both cases a single time constant was found. In order to increase the temperature range of our study the pulse-train method was followed up by DLTS measurements.

V. AUGER-TYPE CAPTURE PROCESSES

To demonstrate the different types of capture processes for holes at the D^0 and D^+ centers, we will now describe the DLTS measurements in more detail using selenium-doped n^+p diodes as an example. The capture of holes at Se^0 and Se^+ centers was studied by first applying a minority-carrier pulse to establish a certain electron occupancy of the centers, followed by a majority-carrier pulse. The length of the majority-carrier pulse was increased in subsequent DLTS runs (Fig. 6). For a majority pulse length of 2 ms, the electron occupancy of the Se^0 center was almost negligible, while the occupancy of the Se^+ center was about 50%. Plotting the logarithm of the height of the two DLTS peaks obtained for a particular rate window as a function of the majority-carrier pulse length gives similar time constants for both the Se^0 and Se^+ peaks (Fig. 7). Furthermore, these time constants were very close to the time constant obtained for Se^0 using the pulse-train method (Fig. 5), whereas the time constants obtained for the Se^+ center shown in Figs. 5 and 7 differ by about 7 orders of magnitude. It should be noted that the Se^0 and Se^+ peaks appear at different temperatures. Owing to experimental difficulties it was not possible to decrease the Se^+ peak (Fig. 6) further by increasing the length of the majority pulse. Not even the largest majority pulse length (2.5s) changed the Se^+ peak height. Since the chalcogens form double donors, two DLTS peaks of similar heights are expected if the injection pulses completely fill the D^0 centers with electrons. However, owing to similar capture rates for electrons and holes for the D^0 centers, the highest concentration of D^0

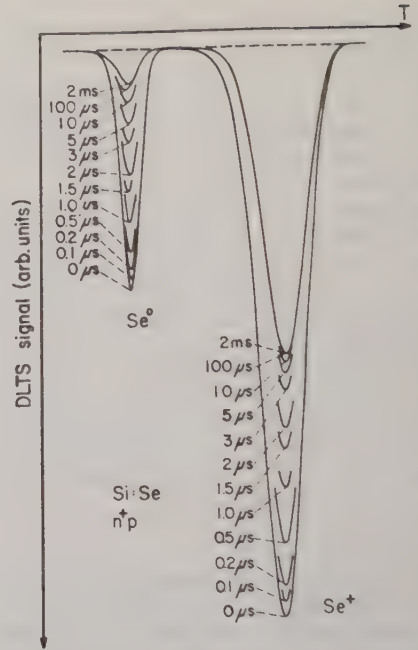


FIG. 6. Hole-capture measurements on a Se-doped n^+p diode showing the decrease in the DLTS peak heights with increasing majority-carrier pulse length. Note that there is no significant decrease in the Se^+ peak when the pulse length is increased from 100 μs to 2 ms.

centers which can be obtained in an n^+p diode after applying a long minority pulse is about one-half the concentration of the D^+ centers. It should be noted that electron capture into the D^{2+} centers is much faster than it is into the D^+ centers, and, hence, D^+ centers could be generated with short minority-charge-carrier pulses without generating any D^0 centers at all.

Very similar results were obtained in sulfur-doped sam-

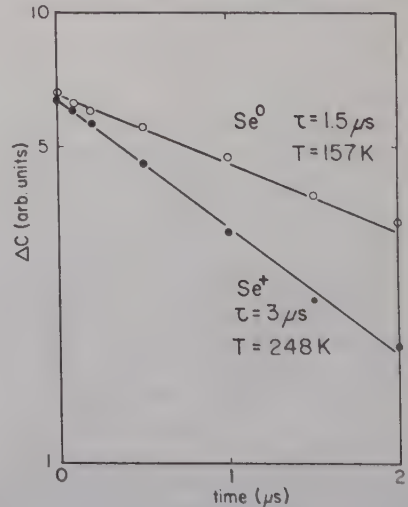


FIG. 7. Plot of the Se^0 and Se^+ DLTS peak heights (Fig. 6) vs the majority-carrier pulse length Δt .

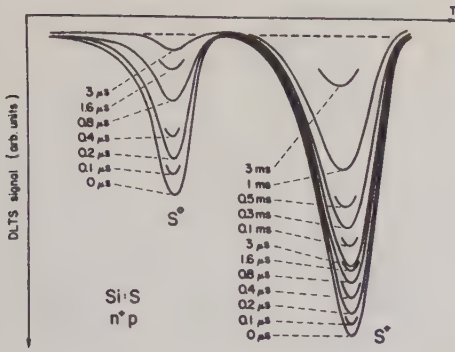


FIG. 8. Hole-capture measurement on a S-doped n^+p diode. Note the "break point" for the S^+ peak for a $3\text{-}\mu\text{s}$ majority-carrier pulse length.

ples, as can be seen by the data presented in Fig. 8 showing the DLTS spectrum of a Si:S sample. The spectrum is almost identical to the Se spectrum, except that the S^+ peak becomes very small for long majority pulses. Whereas the decrease in the S^0 peak is described by one time constant [squares in Fig. 9(b)], the data for the S^+ peak resulted in two time constants [Fig. 9(a)]. The first time constant of Fig. 9(a) was obtained by subtracting the slower part of the decay from the rest of the curve [Fig. 9(b)]. The time constant of the transient obtained [solid circles in Fig. 9(b)] was very close to the time constant of the transient obtained for the S^0 peak [squares in Fig. 9(b)], and the corresponding capture cross sections were almost identical, considering the different temperatures at which the peaks occurred. The second time constant derived from the data presented in Fig. 9(a) was about 3 orders of magnitude larger than the fast time constant and similar to the time constant obtained for S^+ by the pulse-train method.

It should be noted that the D^0 centers were obtained by filling the donors with electrons during the minority-

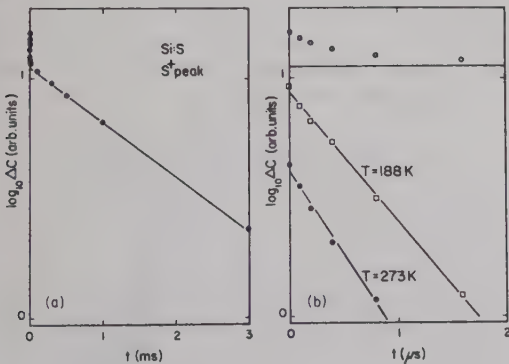


FIG. 9. (a) Biexponential behavior of the S^+ peak (Fig. 8) due to the hole capture at the neutral sulfur center at the temperature given by the S^+ peak (see text). (b) Comparison between the transient of S^0 (squares) and the first part of S^+ (solid circles).

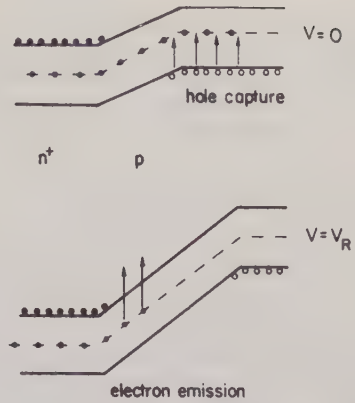


FIG. 10. Simplified figure showing the origin of the residual D^0 DLTS peak (Figs. 6 and 8) still seen for a very long majority-carrier pulse length.

carrier pulse. The capture of holes was then initiated by a majority-carrier pulse. Since minority-carrier injection had to be avoided during the application of the majority-carrier pulse it was not possible to increase the concentration of holes during the application of the majority-carrier pulse in that region of the space-charge region which was closest to the n region (Fig. 10). Since the D^0 centers in this region could not be emptied due to the capture of holes, they always contributed to the DLTS signal irrespective of the length of the majority-carrier pulse. This is the reason why a small D^0 signal in the DLTS spectrum of Figs. 6 and 8 was observed even for very large majority-carrier pulse lengths.

The results presented so far are best understood if it is assumed that the hole capture at a D^0 center results in an annihilation of the associated D^+ center, i.e., that the capture of a hole into a D^0 center simultaneously causes the excitation of the second electron into the conduction band, transforming a D^0 center directly into a D^{2+} center [Eq. (3)]. This type of hole capture is considered an Auger-type hole-capture process,⁷⁻¹⁰ which is possible if the energy released by the hole-capture process exceeds the energy needed to excite the second electron into the conduction band. This Auger-type process does *not* depend on the free-carrier concentration.

In order to obtain further evidence for the Auger-type hole-capture process, additional experiments were performed. The total capacitance C of the diode was studied as a function of temperature T (Fig. 11). The diode was first cooled from room temperature to 77 K under constant reverse bias. After applying a minority-carrier pulse (min. pulse; see Fig. 11) which generated a certain number of D^0 and D^+ centers, the diode was warmed up to room temperature in the first experiment. At temperatures T_1 and T_2 the C - T curve (1) showed two steps owing to the thermal ionization of the D^0 and D^+ centers, respectively. In the second experiment (curve 2) the diode was cooled again to 77 K, but this time a majority-carrier pulse (maj. pulse) was applied at a temperature T_3 directly after the application of the minority-carrier pulse. The pulse length Δt of the majority-carrier pulse was chosen to

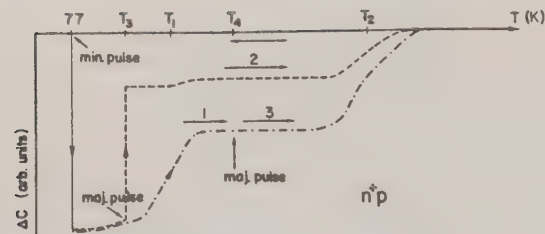


FIG. 11. Junction capacitance vs temperature (see text).

be about ten time constants of the hole capture at D^0 centers in order to ensure that any electron occupancy of D^0 centers could be neglected after the application of the majority-carrier pulse. It should be noted that, owing to the results presented in Figs. 3 and 4, such a majority-carrier pulse is not expected to change the electron occupancy of the D^+ centers. When the temperature was raised, the C - T curve showed only one step at T_2 owing to the ionization of those D^+ centers which were generated by the minority-carrier pulse in excess of the D^0 centers. Some D^0 centers close to the n region (Fig. 10) remain occupied by electrons after the majority-carrier pulse and give rise to a small step in the C - T curve (Fig. 11, curve 2). The experiment clearly showed that owing to the majority-carrier pulse the diode capacitance decreased by almost twice as much as in the first experiment due to the thermal ionization of the D^0 centers.

In order to show that this decrease in capacitance was not caused by hole captures into D^+ centers, a third experiment was performed (curve 3). After cooling the diode to 77 K and applying a minority-carrier pulse, the majority-carrier pulse was first applied at temperature T_4 after the D^0 centers were already completely ionized. No change in the C - T curve was observed compared with the first experiment, showing that the majority-carrier pulse length Δt was sufficiently short to not significantly change the occupancy of the D^+ centers. This sequence of experiments clearly demonstrates the Auger-type capture process, since in the absence of the Auger process the capacitance is expected to decrease due to the majority-carrier pulse in the second experiment by the same amount as in the first experiment. Furthermore, the experiments clearly show that the centers studied are double donors, i.e., that the D^0 , D^+ , and D^{2+} centers are three different charge states of the same defect.

These experiments could be performed in both sulfur- and selenium-doped silicon diodes, but not in tellurium-doped samples because of the high electron-emission rate of the Te^0 centers at 77 K and the freeze-out of the shallow-acceptor levels in the p region below 77 K.

Since our experiments unambiguously demonstrated that the D^0 , D^+ , and D^{2+} centers are different charge states of the same defect it should be possible to obtain information on one of these centers by measuring certain properties of the other center. It has already been shown that hole capture into D^0 centers resulted in the annihilation

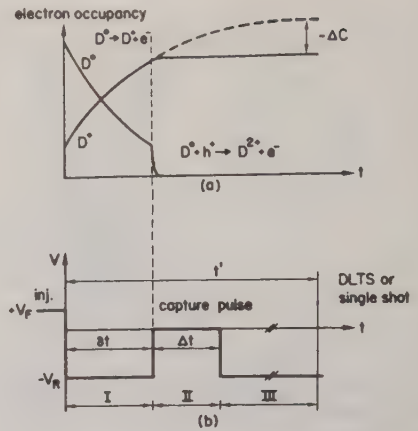


FIG. 12. Time dependence of the occupancies of the D^0 and D^+ centers owing to the pulse sequence shown in (b). Because of different final charge states obtained by electron emission and Auger hole capture at D^0 different occupancies of D^+ are obtained for varying time delays δt .

tion of a similar number of D^+ centers. This gives us the possibility of measuring the hole-capture process for D^0 by studying the D^+ DLTS peak. Furthermore, the decrease in the D^+ signal of the DLTS measurements due to the majority-carrier pulse, i.e., hole capture into D^0 , can therefore be considered as a measure of the concentration of D^0 centers at this particular temperature and time, δt . After applying the minority-carrier pulse the occupancy of D^0 centers at a particular temperature is, however, time dependent owing to the thermal ionization of D^0 centers. The time dependence of the occupancy of D^0 centers at a particular temperature can therefore be measured in different DLTS experiments by using constant rate windows but varying the time delay, δt , between the minority-carrier pulse and the majority-carrier pulse of constant length Δt (Fig. 12). The pulse length (Δt) was chosen to be sufficiently short to ensure that no holes were captured into the D^+ center during the majority-carrier pulse. Hence, plotting the decrease in the DLTS signal of the D^+ peak (Fig. 13) logarithmically against the time delay δt should result in a straight line (Fig. 14),

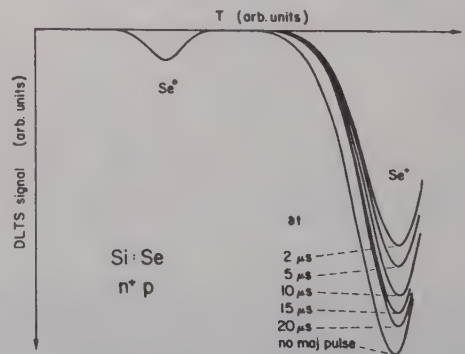


FIG. 13. DLTS spectra obtained for different time delays δt .

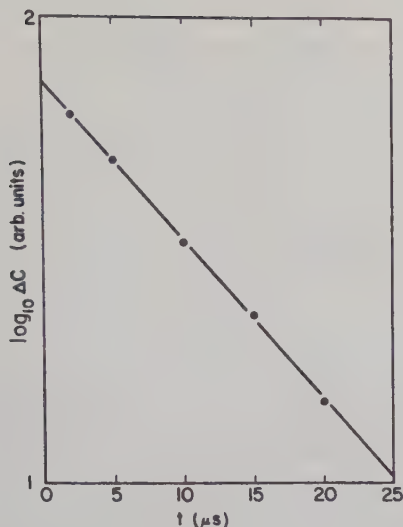


FIG. 14. Plot of D^+ peak in Fig. 13 vs time delay δt .

the slope of which corresponds to the thermal emission rate for electrons of the D^0 center at the temperature given by the DLTS peak of the D^+ signal. By varying the rate windows and, hence, shifting the peak temperature of the D^+ signal, the thermal emission rate for electrons, e_n' , of the D^0 centers, can be measured as a function of temperature and can be compared with previous measurements (Fig. 2) of $e_n'(D^0)$ obtained with conventional techniques. Similar measurements were performed using a single-shot capacitance method. The thermal emission rates of electrons obtained for the S^0 , Se^0 , and Te^0 centers, by studying the D^+ peaks at different temperatures, are plotted in Fig. 15, together with our data previously presented in Fig. 2. The results clearly show that the indirect measurements give the same activation energies as

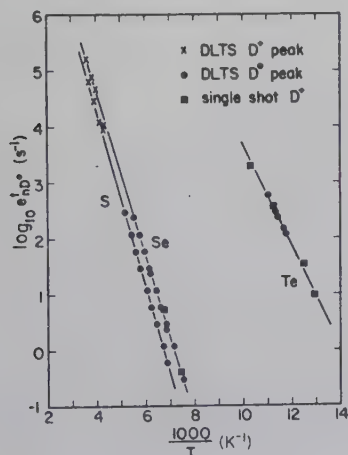


FIG. 15. Comparison of thermal emission data obtained with conventional methods (solid circles) and with the method explained in Fig. 12 (crosses and squares).

already obtained by more conventional techniques. The experiments once more confirm the different charge states of a double donor and the existence of the Auger-type hole-capture process. Without any of these properties, the above results could not have been obtained.

VI. DISCUSSION

Auger capture processes at He-like centers have been discussed previously in the literature⁷⁻¹⁰ and are expected to be the dominant capture process for such types of centers. However, to the best of our knowledge only very few cases are described in the literature in which this type of capture process has been studied experimentally. Non-radiative capture processes are generally explained by either multiphonon emission or cascade processes. In both cases the capture cross section shows a typical temperature dependence. The capture cross sections obtained for MPE processes are often rather small and increase with temperature, whereas those observed for cascade processes can be large and decrease with temperature. The results presented in this paper show that Auger-type capture processes may, in principle, result in rather large or at least—as in our case—moderately large capture cross sections which exhibit a weak temperature dependence. Similar chemical trends are observed for both σ_{pD^0} and σ_{pD^+} , implying that the sulfur center has the largest capture cross section for holes and the tellurium center the smallest. This result is in agreement with previous theoretical considerations⁷⁻¹⁰ of Auger-type capture processes, showing that σ_{pD^0} should increase with increasing binding energy of the centers if effective-mass-like wave functions are used. It has also been predicted that the capture cross section should only be weakly temperature dependent, in agreement with the results obtained for σ_{pD^0} and presented in Fig. 4.

Since double donors (and acceptors) exist not only in silicon but probably also in other materials such as III-V compounds, it may be possible that such centers contribute to nonradiative recombination processes to a much greater extent than hitherto appreciated.

In contrast to σ_{pS^0} , the hole-capture cross section of S^+ showed a rather pronounced temperature dependence and increased with increasing temperature. This may suggest that the hole-capture process at S^+ centers is governed by a kind of MPE process. MPE-governed capture processes have two temperature limits. At high temperatures the capture cross section approaches an exponential behavior, whereas at low temperatures the cross section is almost temperature independent. A theoretical model has been developed previously,¹⁴ describing the temperature dependence of MPE-governed capture processes. The model includes two adjusting parameters, the capture barrier height and the dominant phonon energy. Fitting the experimental results obtained for σ_{pS^+} to this model (Fig. 16), a barrier height of about 147 meV and a phonon energy of 18.4 meV are deduced. This implies a large Franck-Condon shift of about 0.2 eV. Considering that the model is very sensitive to the value of the fitting parameters and that previous optical spectra¹⁵ did not show

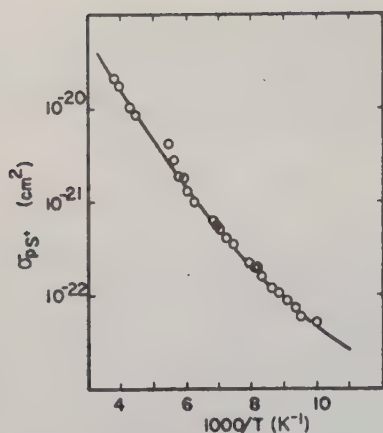


FIG. 16. Hole-capture cross section of S^+ (circles) fitted to the MPE model of Ref. 11 (solid line).

any indication of such a large Franck-Condon shift, further work is needed for better insight into the hole-capture processes of charged sulfur centers. Fitting our σ_{pS^+} and σ_{pTe^+} data to the same model required a phonon energy of about 60 meV.

It is worth mentioning that the low-temperature values of all σ_{pD^+} cross sections are of the same order of magnitude as the radiative capture cross sections $\sigma_{pD^+}^r$ obtained from the photoionization cross section $\sigma_{pD^+}^0$ using the

principle of detailed balance.¹⁶ $\sigma_{pD^+}^r$ is expected to be proportional to $\sigma_{pD^+}^0$ when neglecting the small difference in the binding energies of S^+ and Se^+ . It is interesting to note that previously published values of $\sigma_{pD^+}^0$ (Ref. 15) for S and Se indeed show a similar trend as the corresponding hole-capture cross sections. We have no further information on whether the hole-capture process at neutral chalcogen centers is indeed radiative. The properties of chalcogen-doped silicon devices will be discussed in a forthcoming paper.¹⁷

VII. SUMMARY

We have presented experimental evidence for Auger-type capture processes at He-like defects in semiconductors. The temperature dependence and the absolute values of the Auger capture cross sections are in agreement with theoretical estimates. Our results clearly show that the D^0 and D^+ centers are neutral and singly positively charged versions of a double donor. The hole capture at S^+ has been discussed in terms of MPE processes and a combination of MPE and radiative capture processes. The results obtained for the hole-capture process at Se^+ and Te^+ centers are (in the temperature region studied) close to values expected for radiative capture process.

ACKNOWLEDGMENTS

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RECOMBINATION AND GENERATION PROCESSES IN SELENIUM-DOPED SILICON

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ABSTRACT

The generation and recombination properties of selenium in silicon have been investigated. Arrhenius plots of the reverse dark current ($\log I - 1/T$) gave the same "thermal activation energy" for both selenium-doped and reference diodes indicating that some other mechanisms than generation at selenium centres are responsible for the reverse current. The magnitude of the reverse current showed that previously published data on hole emission from doubly ionized selenium double donors must be at least one order of magnitude too high. Lifetimes of excess charge carriers have been calculated showing that the two-electron level of selenium double donors is responsible for recombination in n-type silicon.

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I INTRODUCTION

Deep-level impurities have frequently been used to control the lifetime of excess charge carriers in semiconductor devices. Gold and later platinum have been successfully employed in switching devices. Many other deep-level impurities have therefore been investigated through the years and some of them show interesting properties.

Recently, increasing interest has been paid to chalcogen, S, Se, and Te, impurities in silicon. Chalcogens give rise to several deep centres in silicon. An isolated, substitutional, S, Se, or Te atom forms a double donor in silicon [1] which gives rise to two energy levels in the band gap. The neutral donor state, corresponding to the shallower level, has recently been shown to act as an efficient recombination centre [1,2]. The hole capture is governed by an Auger process [1]. The electron-capture process has been investigated for S and Se and been shown to be a cascade, or at least a two-stage, process via excited states [2,3]. The Auger hole-capture cross-sections have been shown to be almost temperature independent [1] in accordance with the results of theoretical studies [4-7].

In the case of selenium, the Gibbs free energy of the two donor levels, labelled Se(2) and Se(1), are $E_C - 0.28$ eV and $E_C - 0.52$ eV [2], respectively. The hole-capture cross-section for Se(2) is about $\sigma_p = 7 \cdot 10^{-17} \text{ cm}^2$ at room temperature. The electron-capture cross-section is given by the expression [2]

$$\sigma_n = 6.24 \cdot 10^{-9} T^{-3.16} (\text{cm}^2) \quad (1)$$

which at room temperature gives $\sigma_n = 9 \cdot 10^{-17} \text{ cm}^2$.

These examples are presented to show the magnitude of actual cross-sections.

Since chalcogens may be interesting impurities for controlling the lifetime of excess charge carriers it is the purpose of this paper to investigate the recombination and generation properties of the selenium double donor in silicon in more detail.

II GENERATION CURRENT

The dark-current density of a reverse-biased pn junction given in [8]

$$J_R = q \int_{x_1}^{x_2} [1/D \cdot U_n + (1 - 1/D) \cdot U_p] dx \quad (2)$$

for a single energy level, must be extended in the case of double donors to

$$J_R = J_{R1} + J_{R2} = q \int_{x_{11}}^{x_{21}} [1/D \cdot U_{n1} + (1 - 1/D) \cdot U_{p1}] dx + \\ q \int_{x_{12}}^{x_{22}} [1/D \cdot U_{n2} + (1 - 1/D) \cdot U_{p2}] dx \quad (3)$$

The indices 1 and 2 refer to the one- and two-electron level of the double donor, respectively. $x_2 - x_1$ is the effective width of the generation region [8]. U_n and U_p are the total net emission rates (per unit volume) of electrons and holes, respectively. D is the ratio between the excited charge within the effective generation region

$x_2 - x_1$ and the measured charge in the external circuit [9]. Since capture processes can be neglected in reverse-biased pn junctions, the net emission rates (per unit volume) of electrons and holes are given by:

$$U_{n1} = e_{n1} n_{T1} \quad (4)$$

$$U_{p1} = e_{p1} p_{T1} \quad (5)$$

$$U_{n2} = e_{n2} n_{T2} \quad (6)$$

$$U_{p2} = e_{p2} p_{T2} \quad (7)$$

where p_{T1} is the density of the doubly ionized donors, $n_{T1} = p_{T2}$ is the density of the singly ionized donors and n_{T2} is the density of the neutral donors. The total concentration of double donors can then be expressed as

$$N_{TT} = p_{T1} + n_{T1} + n_{T2} \quad (8)$$

Substituting Equations (4-7) into Equation (3) yields, for a reverse bias $V_R \gg kT/q$:

$$J_R = J_{R1} + J_{R2} = q[x_2 - x_1] \left[\frac{1}{D} e_{n1} n_{T1} + (1 - \frac{1}{D}) e_{p1} p_{T1} \right] + q[x_2 - x_1] \left[\frac{1}{D} e_{n2} n_{T2} + (1 - \frac{1}{D}) e_{p2} n_{T1} \right] \quad (9)$$

If free charge carrier tails extending from the neutral region into the space-charge region, are neglected, D can be approximated by a value of 2.

In Appendix A, the expressions for p_{T1} , n_{T1} and n_{T2} are derived. Neglecting capture processes in the depletion region, it is readily shown, from Equations (19) and (20), that at steady state

$$e_{n2} n_{T2} = e_{p2} n_{T1} \text{ and } e_{n1} n_{T1} = e_{p1} p_{T1}. \text{ Equation (9) then reduces to}$$

$$J_R = J_{R1} + J_{R2} = q[x_{21} - x_{11}]e_{p1}p_{T1} + q[x_{22} - x_{12}]e_{p2}n_{T1} \quad (10)$$

Recent data [2] show that the emission rate of holes (e_{p1}) is about two orders of magnitude lower than for electrons (e_{n1}) for the one-electron level, Se(1). Our results show that the hole emission rate is even lower. Consequently, $p_{T1} = N_{TT}$ and n_{T1} is small. Furthermore, since e_{p2} probably is much smaller than e_{p1} , the term J_{R2} , due to the emission processes from the two-electron level Se(2), may then be neglected in Equation (9).

Thus, Equation (9) reduces to a simple expression.

$$J_R = J_{R1} = q(x_{21} - x_{11})N_{TT}e_{p1} \quad (11)$$

Equation (11) shows that the dark current for a selenium-doped pn diode is proportional to the number of double donors in the space-charge region and the hole-emission rate for the one-electron level, Se(1).

p^+n diodes, with an area of 0.4mm^2 , having an arsenic-doped epitaxial layer with a net donor concentration of $N_D = 6.6 \times 10^{15}\text{cm}^{-3}$ (deduced from $C^{-2}-V$ measurements), were used to study the dark current. The diodes were then selenium-doped to a double-donor concentration of $n_T = 8.8 \times 10^{14}\text{cm}^{-3}$, as calculated from DLTS (Deep-Level Transient Spectroscopy) [10] measurements (Figure 1). Due to the selenium doping the net donor concentration increased to $N_D = 1.1 \times 10^{16}\text{cm}^{-3}$, deduced from $C^{-2}-V$ measurements.

Using Equation (11) and the e_{p1} value from Ref. [2], a dark-current of about $I_R = 10^{-10}$ A was calculated when using a reverse bias of 20 V at room temperature. However, under these conditions our selenium-doped diode showed a dark current of only 10^{-11} A, which was about the same as the dark current of the reference diode without selenium. The I-V characteristics for these diodes are presented in Figure 2.

It must be stressed that these measurements were carried out on the best diodes we were able to produce and we could not establish any reproducible differences between the selenium-doped and the reference diodes. The value of the reverse dark current was unique for every diode and very sensitive to the low-temperature heat treatment e.g. during mounting on the TO-5 header. This observation may indicate that the origin of the reverse dark current is due to other excitation processes than via selenium-related centres.

However, if it is assumed that the reverse dark current originates from a generation current via the selenium centres, it follows from Equation (11) that the reverse dark current should be proportional to e_{p1} given by [11].

$$e_{p1} = \sigma_{p1} \langle v_{TH} \rangle N_V e^{-\delta G_p / kT} \quad (12)$$

Here σ_{p1} is the hole-capture cross-section for the one-electron level and δG_p is the change in Gibbs free energy when exciting an electron from the valence band to Se(1). Hence, by plotting the reverse dark current in an Arrhenius plot, an activation energy should be obtained reflecting the energy distance between the one-electron level Se(1) and the valence band. The results are presented in Figure 3, where the dark current of a selenium-doped and a reference diode are plotted.

Almost identical energies are obtained for the selenium-doped and the reference diode.

The hole-capture cross-section for the one-electron level is $\sigma_{p1} = 10^{-23} \text{ cm}^2$ at 167 K [1]. The hole-emission rate calculated from Equation (12) and using the energy value from Ref. [2] for δG_p is then approximately $e_{p1} = 10^{-17} \text{ s}^{-1}$. The e_{p1} value for $T = 167 \text{ K}$, extrapolated from Ref. [2], is about 10^{-8} s^{-1} which is 9 orders of magnitude higher than the value calculated using Equation (12).

This indicates that the process presented as hole emission in Ref. 2 obviously does not originate from hole emission at Se(1) centres, but rather from charge carrier generation at some other centres. The fact that the activation energies for the reverse dark current of our diodes and for the emission process in Ref. [2] correspond to mid-gap centres, indicates similar current sources. Mid-gap centres can be found among surface states [12].

We conclude that selenium does not act as the dominant generation centre in our silicon diodes because of the relatively small emission rates of holes for both Se(2) and Se(1), and that the measured reverse dark current is not due to excitation via the Se(1) level.

III RECOMBINATION

The treatment of recombination processes via selenium double donors in silicon must deal with multiple-level statistics [11].

At steady-state conditions for an n-type semiconductor i.e. $n_0 \gg p_0$, the common lifetime, τ , for excess charge carriers, $\delta n = \delta p$, is given by the expression [11]

$$\tau^{-1} = \sum_{j=1}^2 \frac{(1+h)c_{nj}c_{pj}(n_{Tj} + p_{Tj})}{c_{nj}(1+h+n_j/n_0) + c_{pj}(p_0/n_0 + h + p_j/n_0)} \quad (13)$$

Where $h = \delta n/n_0$.

The low- and high-injection lifetimes, denoted by τ_L and τ_H , respectively, are found by letting $h \rightarrow 0$ and $h \rightarrow \infty$, respectively:

$$\tau_L^{-1} = \sum_{j=1}^2 \frac{c_{nj}c_{pj}(n_{Tj} + p_{Tj})}{c_{nj}(1+n_j/n_0) + c_{pj}p_j/n_0} \quad (14)$$

$$\tau_H^{-1} = \sum_{j=1}^2 \frac{c_{nj}c_{pj}}{c_{nj} + c_{pj}}(n_{Tj} + p_{Tj}) \quad (15)$$

Using a similar approach for p-type silicon it is easily shown that Eqn. (15) is still valid, while the expression for τ_L^{-1} is modified to

$$\tau_L^{-1} = \sum_{j=1}^2 \frac{c_{nj}c_{pj}(n_{Tj} + p_{Tj})}{c_{nj}n_j/p_0 + c_{pj}(1+p_j/p_0)} \quad (16)$$

The electron and hole occupancies of the Se(1) and Se(2) centres can be calculated using Equations (22-24) in Appendix A. Inserting the capture rate values from Table 1 it is readily seen that the lifetimes in n-type silicon are completely determined by the two-electron level, Se(2), and are given by the simple expressions:

$$\tau_L^{-1} = \frac{c_{p2}}{1 + n_2/n_0} N_{TT} \quad (17)$$

$$\tau_H^{-1} = \frac{c_{n2} c_{p2}}{c_{n2} + c_{p2}} N_{TT} \quad (18)$$

Using $n_0 = 10^{15} \text{ cm}^{-3}$ the following lifetimes are obtained

$$\tau_L^{-1} \approx 0.7 \cdot 10^{-9} \cdot N_{TT} \text{ (s}^{-1}\text{)}$$

and

$$\tau_H^{-1} \approx 0.5 \cdot 10^{-9} \cdot N_{TT} \text{ (s}^{-1}\text{)}$$

with N_{TT} in cm^{-3} .

In p-type silicon the situation is more complicated for the low level injection case. The hole-capture rate of the one-electron level, Se(1), is extremely low [1] and determines the recombination via this level. The recombination via the two-electron level, Se(2), is on the other hand limited by the low population of this level in p-type silicon. Using Equation (16) and the c_n and c_p values from Table 1 in Appendix A, it can be shown that Se(2) contributes to recombination if $p_0 < 10^{11} \text{ cm}^{-3}$. For $p_0 > 10^{11} \text{ cm}^{-3}$ the low-level lifetime is dominated by the one-electron level, Se(1), and given by the expression

$$\tau_L^{-1} = \frac{c_{p1} p_0}{n_1} N_{TT} = 2 \cdot 10^{-26} p_0 N_{TT}. \text{ Hence, using an acceptor concentration}$$

such that $p_0 = 10^{15} \text{ cm}^{-3}$, a low level lifetime of $\tau_L^{-1} \approx 2 \cdot 10^{-11} N_{TT}$ is obtained.

IV. CONCLUSIONS.

Selenium can be used to control the excess carrier lifetime in silicon, particularly in n-type material. The advantages of using selenium instead of other lifetime-controlling dopants are many. Devices can be easily doped selectively using ion implantation through a photoresist or SiO_2 mask. The generation current is small and can hardly be detected.

The characteristics of selenium-doped devices will be published elsewhere.

APPENDIX A.

The occupancy of states in the band gap can be calculated using the rate equations for capture and emission processes at the centres. In the case of a double donor, where the hole capture to the two-electron level is an Auger process, the steady-state occupancy is given by the following expressions:

$$\begin{aligned} \frac{dn_{T1}}{dt} = 0 = & c_{n1}np_{T1} + e_{p1}p_{T1} - e_{n1}n_{T1} - c_{p1}pn_{T1} + e_{n2}n_{T2} - e_{p2}p_{T2} - \\ & - c_{n2}np_{T2} \end{aligned} \quad (19)$$

(If the hole capture to the neutral state was not an Auger process there would be an additional term $(+ c_{p2}pn_{T2})$.)

$$\frac{dn_{T2}}{dt} = 0 = c_{n2}np_{T2} + e_{p2}p_{T2} - e_{n2}n_{T2} - c_{p2}pn_{T2} \quad (20)$$

$$n_{T1} = p_{T2} \quad (21)$$

$$N_{TT} = p_{T1} + n_{T1} + n_{T2} \quad (22)$$

Emission and capture rates are shown in Figure 4.

From Equations (19-22) the occupancy of the states can be easily derived. Thus the electron occupancy of the one-electron level is given by

$$n_{T1} = N_{TT} \left[\frac{e_{p2} + c_{n2}n}{e_{n2} + c_{p2}p} + \frac{e_{p2} + c_{n2}n}{e_{p1} + c_{n1}n} + \frac{e_{n1} + c_{p1}p}{e_{p1} + c_{n1}n} - \frac{e_{n2}(e_{p2} + c_{n2}n)}{(e_{n2} + c_{p2}p)(e_{p1} + c_{n1}n)} + 1 \right]^{-1} \quad (23)$$

and the electron occupancy of the two-electron level is

$$n_{T2} = n_{T1} \frac{e_{p2} + c_{n2}n}{e_{n2} + c_{p2}p} \quad (24)$$

Using values of emission- and capture-rate coefficients summarized in Table 1, the following occupancies at 300 K are obtained.

In p-type silicon with $N_A - N_D = 10^{15} \text{ cm}^{-3}$, under low-injection conditions the electron occupancy of the one-electron level is

$$n_{T1} \approx N_{TT} * 2 * 10^{-4}$$

Under high-level injection conditions e.g. in a forward-biased pn diode with $V_F = 1.0V$, the occupancy is increased to

$$n_{T1} \approx N_{TT} * 0.5$$

In n-type silicon with $N_D - N_A = 10^{15} \text{ cm}^{-3}$, under low-level injection conditions, the electron occupancy of the two-electron level corresponding to the neutral state of the double donor is

$$n_{T2} \approx N_{TT} * 0.56$$

For $N_D - N_A = 10^{16} \text{ cm}^{-3}$ n_{T2} increases to

$$n_{T2} \approx N_{TT} * 0.93$$

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Table 1.

Capture and emission rates used in the calculation of the electron occupancy of the energy levels associated with the selenium double donor in silicon at room temperature.

Level	$e_n (s^{-1})$	$e_p (s^{-1})$	$c_p (cm^3 s^{-1})$	$c_n (cm^3 s^{-1})$
Se ₂	$8 \cdot 10^5$ a)	$\approx 10^{-4}$ b)	$\approx 10^{-9}$ a)	$\approx 10^{-9}$ d)
Se ₁	$6 \cdot 10^2$ d)	$< 10^{-1}$	$\approx 10^{-15}$ c)	$> 10^{-7}$ d)

a) Ref. 1.

b) Calculated using eq. (12) and c_p value for Se(2). This value is an upper limit of e_{p2} since e_{p2} and c_{p2} (in Ref. 1) are not connected through the principle of detailed balance.

c) Ref. 1, extrapolated value.

d) Ref. 2, extrapolated value.

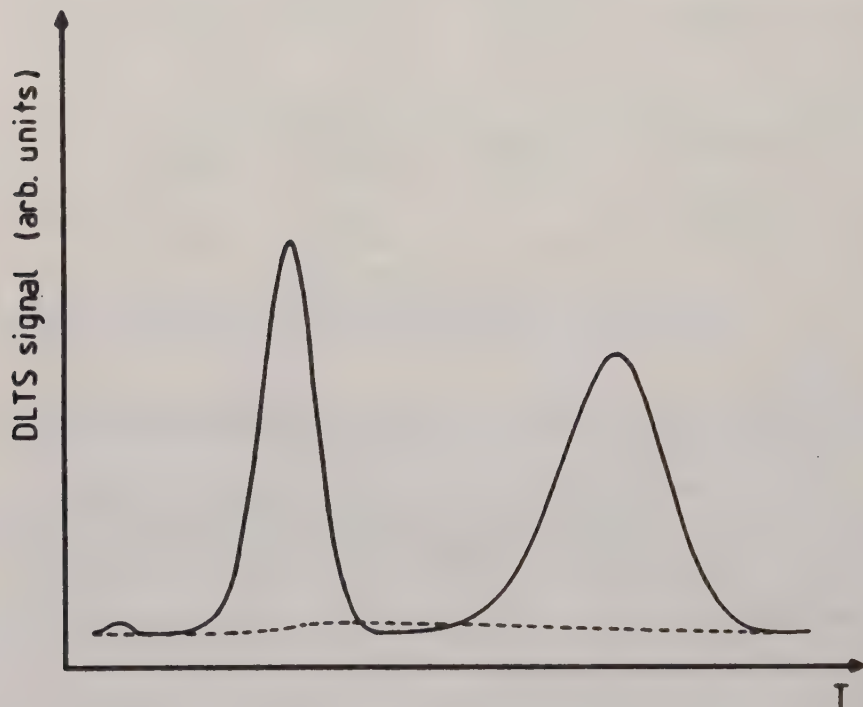


Fig. 1 DLTS spectra of our n^+p diodes. Solid curve: selenium doped diode, dashed curve: reference diode (measured with 10 times higher sensitivity than the selenium-doped diode).

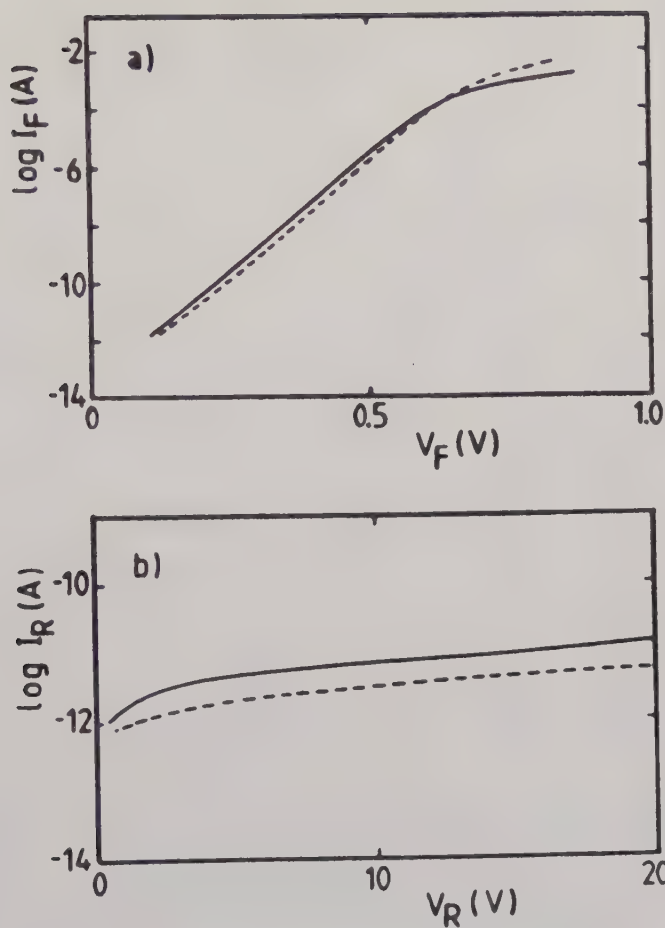


Fig. 2 I-V characteristics of n^+p diodes: a) forward, b) reverse. Solid curve: selenium-doped diode, dashed curve: reference diode.

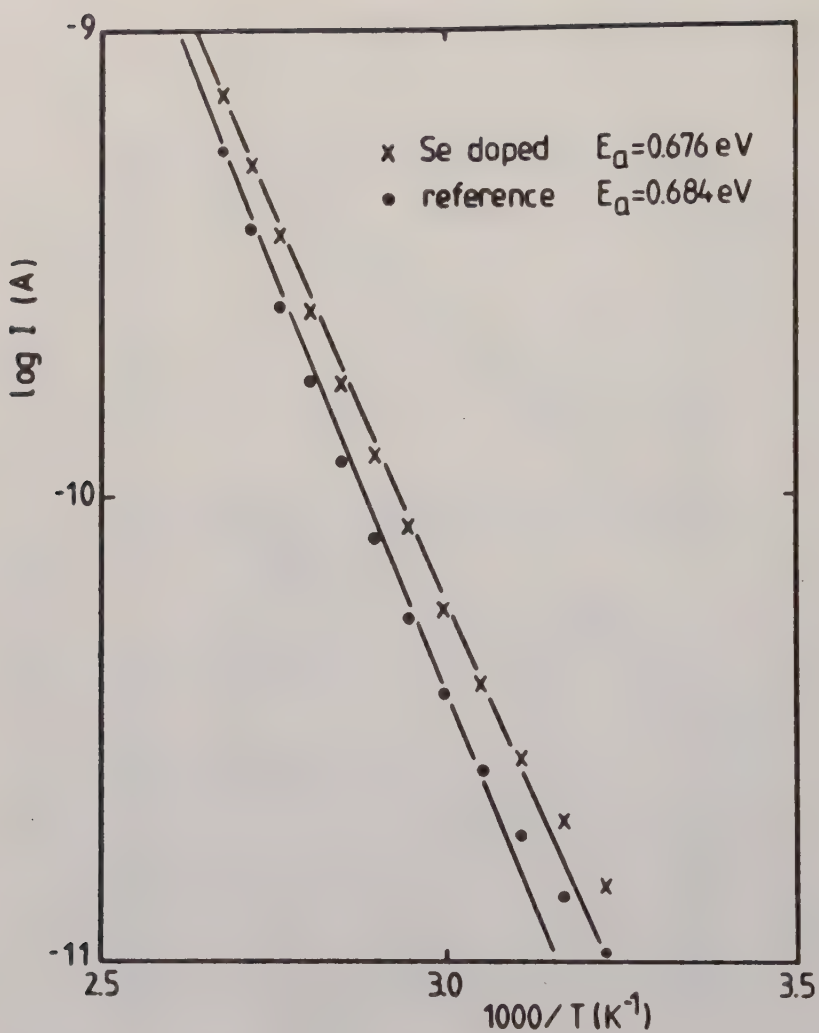


Fig. 3 Dark reverse current vs inverse temperature for selenium-doped and reference diodes. The activation energy, E_a , of the process is obtained from the slope of the curves.

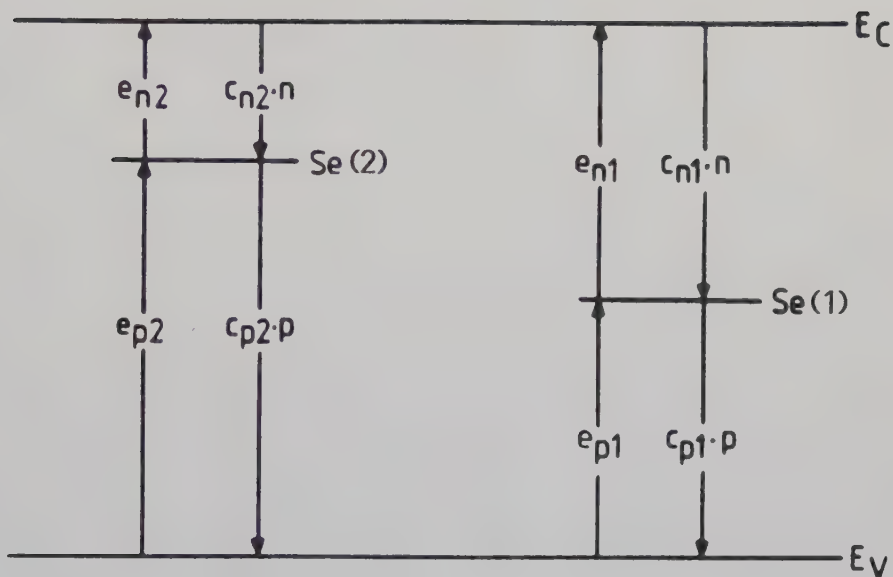
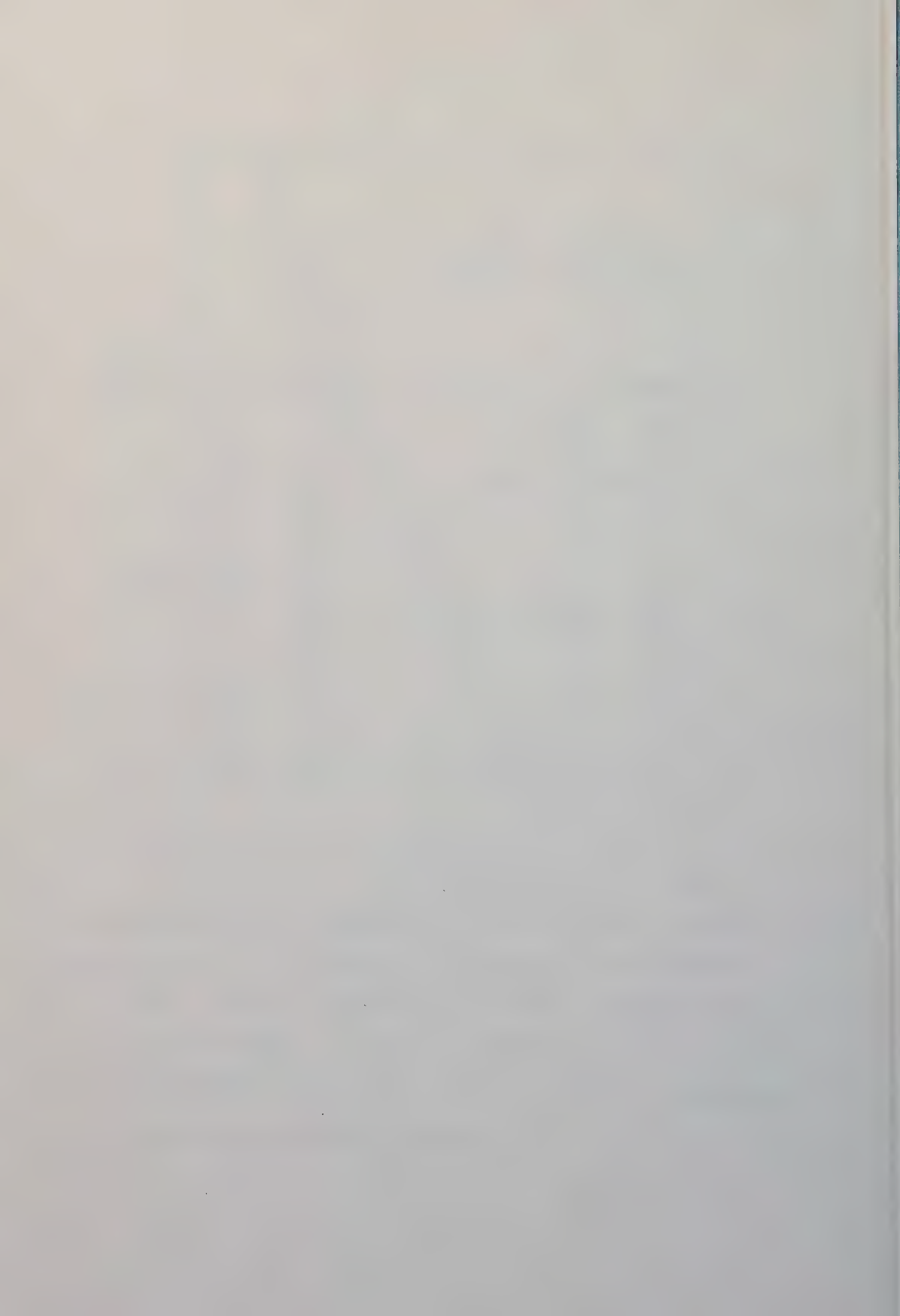


Fig. 4 Capture and emission coefficients associated with the capture and emission processes at the selenium double donor.



PROPERTIES OF SELENIUM-DOPED SILICON NPN TRANSISTORS

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Abstract

The properties of selenium-doped silicon npn transistors have been investigated. Spreading resistance and DLTS techniques were used to establish shallow and deep impurity distribution in the devices. In addition, electrical parameter measurements were performed on the transistors. With increasing selenium doping, the devices showed a decrease in collector saturation current I_S and an increase in base current. These changes were almost uniform for the entire collector current range and are explained as being the result of the presence of selenium deep-level recombination centres and dopant profile redistribution in the devices. The maximum decrease in the current gain, h_{FE} , for selenium-doped transistors was approximately a factor of 4 compared with undoped transistors.

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c_n	thermal capture rate for electrons at a recombination centre.
c_p	thermal capture rate for holes at recombination centre.
h_{FE}	common-emitter DC-current gain
n_0	equilibrium free electron density
n_{p0}	equilibrium free electron density in a p-type semiconductor
n_j	equilibrium free electron density when the chemical potential coincides with the recombination level location
n_T	density of electrons trapped in a centre
p	free hole concentration
p_0	equilibrium free hole density
p_{n0}	equilibrium free hole density in an n-type semiconductor
p_j	equilibrium free hole density when the chemical potential coincides with the recombination level location
p_T	density of holes trapped in a centre
ϵ	dielectric permittivity
μ_n	electron mobility
μ_p	hole mobility
τ_H	high level lifetime
τ_L	low level lifetime
τ_n	electron lifetime
BV_{CBO}	collector-base breakdown voltage
BV_{CEO}	collector-emitter breakdown voltage

BV_{EB0}	emitter-base breakdown voltage
D_n	electron diffusivity
D_p	hole diffusivity
L_B	electron diffusion length in the base
L_p	hole diffusion length
N_B	net acceptor density in the base
N_D	net donor density in the epitaxial layer
N_{TT}	density of recombination centres
Q_b	majority carrier charge in the base
V_{BC}	collector-base voltage
V_{BE}	emitter-base voltage
V_T	thermal voltage
W	base width
ϕ_B	emitter-base junction built-in potential

1. INTRODUCTION

Deep-level impurities have long been considered important in both pure and applied solid-state research because of their influence on free carrier lifetimes in semiconductor devices.

Much work has been done on characterizing devices doped with gold and platinum. However, other deep-level impurities have been investigated with the emphasis placed on their electronic properties.

The introduction of selenium in silicon creates a number of deep-level centres [1,2]. One of these centres is reported to be an isolated double donor [3]. The neutral state of this donor, with a thermal energy level of $E_C - 0.28\text{eV}$, showed to have rather large capture rates [3,4]. The electron capture to this level was shown to be a cascade process or at least a two-stage capture process via excited states [4]. The hole capture is an Auger process [3]. Selenium also gives rise to other energy levels in the energy band gap and may thus affect the free carrier density in silicon [1,5].

The purpose of this paper is to evaluate the characteristics of selenium-doped npn transistors in order to investigate the possibility of applying selenium as a new deep-level dopant in silicon bipolar devices. It will be shown that selenium doping using ion implantation

as an impurity source followed by a by diffusion affects almost every aspect of the transistor static properties. The various transistor parameters have been studied using common measurement methods. The experimental techniques are shortly described in Section 2 and the results obtained by the various methods in Section 3.

2. EXPERIMENTAL DETAILS

2.1 SAMPLE PREPARATION

The npn transistors studied in this paper were parts of integrated bipolar circuits, junction isolated, with a 16 μm thick n-type epitaxial layer with a resistivity of about 3.5 Ωcm . The transistor structure, consisting of an epitaxial collector and diffused base and emitter, is shown in Fig. 1. The base region was formed in two steps. The deep, lightly doped region with a junction depth of approximately 4 μm , was made by ion implantation of boron followed by high-temperature diffusion. The next step consisted of boron deposition from a BCl_3 source followed by diffusion in 1100°C to give a depth of about 2 μm . After base diffusion, windows were opened in the SiO_2 layer to form emitter areas and n^+ collector contacts for npn transistors. These areas were ion-implanted with selenium at 50 keV, using photoresist as an implantation mask. Three different doses were applied : $1 \cdot 10^{15}$, $2 \cdot 10^{15}$, $5 \cdot 10^{15} \text{ cm}^{-2}$, each dose on a quadrant of a wafer. One quadrant was spared for reference transistors. After

implantation, an approximately 2 μm deep layer was formed by phosphorus deposition at 920°C for 20 minutes and diffusion in an oxidizing atmosphere at 1010°C for 50 minutes. A 200 nm CVD SiO_2 layer was deposited and annealed for 40 minutes at 1000°C. The aluminium contacts were sputtered and alloyed for 30 minutes at 450°C in an N_2 atmosphere. The range of selenium implantation at 50 keV is 40 nm, which is negligible in comparison with the emitter depth. During the thermal treatment following the ion implantation the implantation damage was supposed to be healed and due to the high diffusivity [5] selenium diffused throughout the entire transistor structure. The reason for implanting selenium exclusively in the emitter areas was to avoid any residual implantation damage at the base surface. Otherwise, the characteristics of the investigated devices could be affected.

The transistors were too small to perform spreading resistance measurements and therefore some special monitor samples, without any circuit structure, were prepared for such measurements. N-type bulk wafers were prepared in a similar way to the above-mentioned transistors. The wafers were diffused using the same base and emitter processes up to the step of CVD SiO_2 -layer deposition (an npn structure covering an entire wafer with approximately the same diffusion depths as for the transistors). These wafers and further n-type bulk wafers without any additional diffusions were selenium-implanted with a dose of $2 \cdot 10^{15} \text{ cm}^{-2}$ at 100 keV on a part of each wafer. The only reason for using 100 keV instead of 50 keV implantation is the higher achievable implantation current shortening

the long implantation time. The implantation range of 80 nm is still negligible in comparison with the depth of the other diffusions. The non-implanted area was used later as a reference for the monitor samples. The selenium implantation was followed by annealing for 10 minutes in an N_2+O_2 atmosphere and 1 hour in an O_2 atmosphere at $1000^\circ C$. During the annealing process the implantation damage was healed and selenium was diffused deep into the sample structure.

2.2 DLTS MEASUREMENTS

DLTS (Deep Level Transient Spectroscopy) [6] measurements were carried out on the collector-base diode of a large npn transistor to determine the energy levels and the concentrations of the defects created by selenium in the transistor structures. The area of the collector-base junction was 0.19 mm^2 . However, as mentioned before, the selenium-diffusion area was limited by 0.1 mm^2 emitter openings and the defect concentration was adjusted accordingly.

2.3 SPREADING RESISTANCE MEASUREMENTS

The monitor samples, both the selenium-doped and their references, were angle-lapped and the spreading resistance was measured at room temperature as a function of depth (x) into the crystal. From spreading resistance data, the charge carrier concentration was computed. To check the depth of the junctions in the monitor npn structure the samples were ball-ground and stained with concentrated

HF, which coloured the p-doped areas. The junction depth was measured using a Leitz interference microscope with a resolution of $\lambda/2 = 0.275 \mu\text{m}$.

2.4 ELECTRICAL MEASUREMENTS

Electrical properties of the transistors were studied using an HP 4145A Semiconductor Parameter Analyser, a Tektronix 567 Curve tracer and a Boonton 72B capacitance meter.

3. RESULTS AND DISCUSSION

3.1 SELENIUM DIFFUSION INTO TRANSISTORS

3.1.1 Electrical activity.

The spreading resistance measurements were performed on a selenium-diffused n-type monitor sample and an npn monitor structure, as well as on their references, to investigate the dopant redistribution due to selenium diffusion. The charge carrier concentration was computed from the spreading resistance data.

Fig. 2 shows the electron concentrations in the selenium-doped n-type monitor sample and its reference. There is a significant increase in electron concentration at the sample surface, approximately corresponding to the selenium solubility in silicon [5].

This is in accordance with published results [1,5] showing that selenium creates donors in silicon.

Fig. 3 shows the carrier concentration in the npn monitor structure. The most surprising result in the selenium-doped monitor sample is that both the emitter region and the base region are shallower than in its reference. The junction depth changes were confirmed by staining the samples and measuring the depth of the emitter-base and base-collector junctions using an interference microscope.

The transistors were also angle-lapped and stained. The junction depths of the reference transistors were approximately the same as in the reference npn monitor structure.

The free charge carrier concentration was also affected. In the collector, at the base junction, the electron concentrations in the selenium-doped npn monitor sample and in its reference were

$n_0 = 2 \cdot 10^{15} \text{ cm}^{-3}$ and $n_0 = 1 \cdot 10^{15} \text{ cm}^{-3}$, respectively. This ratio of 2 implies an increase in donor concentration in the collector, explaining the cause of the shallower base.

An increased hole concentration, which must be due to an increased acceptor concentration, can be measured in the base region at the emitter junction of the selenium-doped npn monitor sample.

This increased acceptor concentration in the base region was verified by capacitance measurements on transistors. Using the approximation of

a one-sided emitter-base abrupt junction, the capacitance is given by

$$C_{EB} = \frac{\epsilon A}{W} = \left(\frac{q \epsilon N_B A}{2} \right)^{1/2} (\phi_B + v_R)^{-1/2} \quad (1)$$

where N_B is the base acceptor concentration and A is the junction area. The selenium-implanted transistors with doses of 1×10^{15} , 2×10^{15} , and $5 \times 10^{15} \text{ cm}^{-2}$ had capacitances of $C_{EB}(0V) = 114$, 120 , and 140 pF , respectively, while the reference transistor had $C_{EB}(0V) = 98 \text{ pF}$. These values give an idea of the change in the dopant concentration. However, they cannot be used to calculate N_B because of edge effects, contributing to the capacitance of the emitter-base diode. Further, as will be shown in Section 3.2, the emitter-base breakdown voltage and the collector current for different samples indicate an increase in acceptor concentration in the base.

SIMS (Secondary Ion Mass Spectroscopy) measurements were performed on the monitor npn structure. The results [7] showed the phosphorus-emitter retardation and the boron-base diffusion enhancement in the selenium-implanted samples, probably caused by implantation disorder-induced stress [8]. The shallower emitter and the increased acceptor charge in the base are due to these two phenomena.

The conclusion drawn from the measurements described above is that selenium implantation followed by diffusion affects the dopant distribution in transistors. Selenium-related donors increase the doping level in the n-type collectors and implantation effects alter

phosphorus and boron profiles resulting in increased concentration of acceptors in the base region. These conclusions are verified by electrical measurements of npn transistors (Section 3.2).

3.1.2 Deep levels.

Selenium in silicon is reported to give rise to several deep donor levels in the band gap [1]. Two of these have been shown to be a neutral and a singly ionized state of a double donor with thermal activation energy levels of $E_C - 0.28$ eV and $E_C - 0.52$ eV, respectively [4]. The DLTS spectra of the collector-base diode of the various transistors are shown in Fig. 4 together with evaluated concentrations. The activation energies for the levels were $E_C - 0.27$ eV and $E_C - 0.51$ eV, which is very close to the earlier reported values [4].

The concentration, n_T , of the neutral double donors had to be calculated taking the complex device structure into account. Only about one half of the measured junction area, as mentioned in Section 2.2, was selenium doped and this area had a higher donor concentration in the epitaxial layer than the undoped parts. The modified expression [6] used to evaluate n_T is:

$$\frac{n_T}{N_{D2}} \approx \frac{2\Delta C}{C} (1 + (N_{D1}/N_{D2})^{1/2}) \quad (2)$$

where ΔC is the capacitance change due to charge emission from the centres in the depletion zone, C is the total junction capacitance, and N_{D2} and N_{D1} are donor concentrations in selenium-doped and undoped parts of the epitaxial layer, respectively. Calculated values of the epitaxial layer doping are presented in Table 2.

The double donor nature of a substitutional selenium atom in silicon makes it necessary to deal with multiple level recombination statistics to calculate the excess charge carrier lifetime [9]. The low injection lifetime for an n-type semiconductor is given by the expression:

$$\tau_L^{-1} = \sum_{j=1}^2 \frac{c_{nj}c_{pj}(n_{Tj} + p_{Tj})}{c_{nj}(1 + n_j/n_0) + c_{pj}p_j/n_0} \quad (3)$$

and for an p-type semiconductor by

$$\tau_L^{-1} = \sum_{j=1}^2 \frac{c_{nj}c_{pj}(n_{Tj} + p_{Tj})}{c_{nj}n_j/p_0 + c_{pj}(1 + p_j/p_0)} \quad (4)$$

The high injection lifetime τ_H is identical for n- and p-type semiconductors:

$$\tau_H^{-1} = \sum_{j=1}^2 \frac{c_{nj}c_{pj}}{c_{nj} + c_{pj}}(n_{Tj} + p_{Tj}) \quad (5)$$

Using the capture rate values in Table 1, the calculated values of the excess charge carrier lifetime are (for the majority charge carrier concentration $n_0 = p_0 = 10^{15} \text{ cm}^{-3}$ and selenium double donor

concentration $N_{TT} = 10^{14} \text{ cm}^{-3}$ at 300°C):

$\tau_L = 14 \text{ } \mu\text{s}$ for n-type silicon,

$\tau_L = 300 \text{ } \mu\text{s}$ for p-type silicon,

and $\tau_H = 20 \text{ } \mu\text{s}$.

The more common case for p-type silicon with $p_0 = 10^{16} \text{ cm}^{-3}$ and

$N_{TT} = 10^{15} \text{ cm}^{-3}$ yields $\tau_L = 5 \text{ } \mu\text{s}$ and $\tau_H = 2 \text{ } \mu\text{s}$.

3.2 TRANSISTOR CHARACTERISTICS

3.2.1 Collector current.

The npn transistor collector current, restricted to low level injection, can be expressed

$$I_C = I_S (e^{V_{BE}/V_T} - e^{V_{BC}/V_T}) \quad (6)$$

where I_S is the transistor saturation current

$$I_S = \frac{q^2 A n_i^2 V_T}{q \int \frac{p}{\mu_n} dx} \quad (7)$$

where A is the base cross-sectional area, $V_T = \frac{kT}{q}$ is the thermal voltage and, μ_n is the electron mobility in the base.

Most authors [10,11,12] use an average value of the mobility. With this approximation, Eqn. (7) simplifies to

$$I_S = \frac{q^2 A n_i^2 \mu_n V_T}{Q_b} \quad (8)$$

where Q_b is the majority carrier charge in the base, given by

$$Q_b = Q_{b0} - Q_{be} - Q_{bc}, \quad (9)$$

as shown in Fig. 5.

The Gummel plots of various transistors are shown in Fig. 6. It is clear that the collector current I_C decreases with increasing selenium dose. The collector current curves are parallel and the application of Eqn. (6) shows that the saturation current I_S decreases. The implication is that the denominator in Eqn. (7)

$$q \int_{x_{j1}}^{x_{j2}} \frac{p}{\mu_n} dx = \frac{Q_b}{\mu_n} \quad (10)$$

increases with selenium doping, since the remaining terms are constant. Assuming a constant electron mobility the decrease in

collector current is due to an increased acceptor charge Q_{b0} in the base of selenium-doped transistors. This is in agreement with the results of spreading resistance measurements (see Section 2.1.1).

3.2.2 Base current.

The Gummel plots in Fig. 6 show that the base current increases with increasing implanted selenium dose. It will be shown that this effect cannot be completely due to Shockley-Read-Hall recombination in the neutral base region.

The base transport factor, for the short base, is

$$\alpha_T = \frac{J_n(x=W)}{J_n(x=0)} = \frac{1}{\cosh(W/L_B)} \approx 1 - \frac{W^2}{2L_B^2} \quad (11)$$

If the electron diffusion length in the base, $L_B = (D_n \tau_n)^{1/2}$, is short, a reduction in the base width, W , should give a significant rise in α_T , yielding a smaller base current I_B . The change in W is most easily achieved by depleting the base by applying a collector-base reverse bias.

The base current, $I_B = f(V_{BC})$, plotted in Fig. 7, shows that there is instead the opposite effect, except for the highest voltages where the transistors are approaching the avalanche region.

Calculations confirm the results of the above experiment. Using the electron lifetime value $\tau_L = 5 \mu s$ (Section 3.1.2), the diffusion length for electrons, L_B , is found to be $110 \mu m$. This is about two orders of magnitude higher than the base width, W , of about $1 \mu m$.

The observed increase in the base current for selenium-doped transistors cannot solely be the result of the recombination-generation current in the emitter-base depletion region. Such recombination should give a relatively higher base current for small collector currents than for large currents, which is apparently not the case. The described base current behaviour is explained by the increased hole injection into the emitter, given by the well known relation

$$J_p = \frac{q D_p p_{n0}}{L_p} (e^{V_{BE}/V_T} - 1) \quad (12)$$

The spreading resistance measurements did not show any decrease in electron concentration n_{n0} in the emitter of the selenium-doped

transistors. This would result in an increase in $p_{n0} = \frac{n_1^2}{n_{n0}}$. Thus the

increase in J_p must be caused by the shorter hole diffusion length,

L_p , in the emitter.

The effect of the increased base current for selenium-doped transistors is even more accentuated for transistors operating in the inverse mode (the epitaxial layer as emitter). The Gummel plots for various inverse transistors are shown in Fig. 8. The base currents for small collector currents are very similar for all transistors. This result indicates recombination mechanisms other than recombination via selenium donors, e.g. surface recombination could be responsible for the base current in this collector current region. An increase in base current in selenium-doped samples can be observed at higher collector currents, which again can be attributed to the increased hole injection into the emitter (this time consisting of the epitaxial layer).

It should be stressed that the higher donor concentration in the epitaxial layer of selenium-doped devices (as mentioned in Section 3.1.1) is expected to give the opposite effect (a smaller base current). An increase in n_{n0} in Eqn. (12) results in a decrease in the

value of J_p , since $J_p \sim p_{no} = \frac{n_i^2}{n_{n0}}$.

A possible explanation of the observed increase in the base current could be the presence of dislocations extending beyond the collector junction. Ion implantation, followed by drive-in in an oxidizing atmosphere can produce such dislocations. However, a dislocation etch of selenium-doped transistors revealed no such defects.

The conclusion must be that selenium does not significantly affect the diffusion length for electrons in the p-type transistor base, but does affect the diffusion lengths for holes in n-type emitter and collector. This is in accordance with the knowledge that selenium forms efficient recombination centres in n-type silicon [3].

3.2.3 Collector-base diode.

The I-V characteristics for all samples are plotted in Fig. 9. The reverse current is not affected by selenium diffusion. It will be shown elsewhere [13] that selenium does not create efficient generation centres in silicon.

The forward current increases with increasing implanted selenium dose. Using the same arguments as in the previous section this result can be accounted for by the increased hole diffusion into the collector because of the decrease of the hole lifetime in n-type silicon with selenium-generated recombination centres.

In the case of a planar transistor, the breakdown voltage is limited by the curvature radius and dopant concentration at the base corners. In our experiment the transistors were not selenium doped in this area and the collector-base breakdown voltage was not affected by selenium diffusion. The breakdown voltage was about 90V for all samples.

3.2.4 Collector-emitter breakdown voltage.

The empirical expression for collector-emitter breakdown voltage is given by [14]

$$BV_{CEO} = \frac{BV_{CBO}}{(h_{FE} + 1)^{1/n}} \quad (13)$$

where n adopts the value of 4 for an npn transistor and BV_{CBO} is the collector-base breakdown voltage for a plane pn junction. Given BV_{CEO} and h_{FE} , the net impurity concentration in the collector region can be determined using the relation between BV_{CBO} and the impurity concentration [15,16]. BV_{CBO} is calculated from Eqn. (13).

For the reference sample there is excellent agreement between the value of the donor concentration calculated using the above method and the value measured in the epitaxial layer during sample fabrication (see Table 2).

Table 2 shows the h_{FE} , BV_{CEO} , and the calculated donor concentration values for the measured samples. Table 3 shows the relative concentration of the additional donors introduced by selenium diffusion, calculated with the aid of the above method and from DLTS measurements.

3.2.5 Emitter-base breakdown voltage.

In the case of the emitter-base junction, the breakdown occurs at the surface where the impurity concentration is at its highest. The voltage value is mainly dependent on the base doping level. Fig. 10 shows BV_{EBO} for different samples. The lowest BV_{EBO} value is obtained for the highest selenium dose, demonstrating again the increased acceptor concentration in the base of selenium-doped transistors.

It also shows that the increase of the acceptor concentration in the base must be significant at the base surface in order to affect the original surface acceptor concentration, which was determined to be in excess of 10^{18} cm^{-3} .

4. CONCLUSIONS

The effects of ion implantation of selenium, followed by diffusion, on silicon epitaxial npn transistors have been presented in this paper.

As expected, the introduction of selenium into silicon transistors increased the donor concentration in the n-type epitaxial collector, thus compensating the p-type base region and making it shallower. Selenium-related recombination centres decreased the diffusion length for holes in n-type emitters and collectors.

Even the emitter (phosphorus) and base (boron) profiles were altered by selenium ion implantation. Emitter diffusion was retarded and base

diffusion was enhanced resulting in shallower emitter and increased acceptor charge in the base region.

The static characteristics of selenium-doped transistors were affected in almost every aspect. Despite the introduction of recombination centres, the current gain was appreciable even for very low collector currents (h_{FE} larger than 5 at $I_C = 1$ nA) and the reverse-bias current was not larger in selenium-doped than in the reference devices.

These results encourage further investigations in both pure and applied fields. Considering basic properties continued studies of the physical implications of the introduction of selenium and other chalcogens in silicon devices are indispensable. For the application of these results closer analyses are needed to settle open questions such as those concerning dynamic properties, the noise level and long-term stability of the transistors. For several applications selenium doping could be employed to increase the switching performance of npn transistors.

Acknowledgments

I would like to thank Dr M. Kleverman for valuable discussions and T. Pihl from the Microwave Institute in Stockholm for performing the ion implantations. The valuable assistance of Prof. H.G. Grimmeiss during the course of this work is gratefully acknowledged.

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Table 1. Capture rates used for the calculations of the excess charge carrier lifetimes.

c_{n1}	c_{p1}	c_{n2}	c_{p2}
$(\text{cm}^3 \text{s}^{-1})$	$(\text{cm}^3 \text{s}^{-1})$	$(\text{cm}^3 \text{s}^{-1})$	$(\text{cm}^3 \text{s}^{-1})$
Value at 300K $>10^{-7}$ a)	10^{-15} b)	10^{-9} c)	10^{-9} d)

a) ref.4

b) ref.3, extrapolated value

c) ref.4, extrapolated value

d) ref.3, extrapolated value

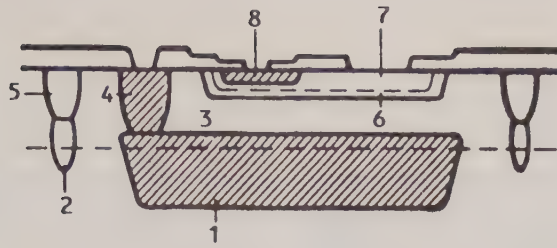
Table 2. Current gain h_{FE} , collector-emitter breakdown voltage and calculated donor concentration, N_D , in the epitaxial layer.

a) N_D value measured in the fabrication process.

Sample	h_{FE}	BV_{CEO} (V)	N_D (cm^{-3})
Se dose (cm^{-2}) ($I_C=100\mu A$, $V_{BC}=-5V$)		($I_C=100\mu A$)	
reference	190	59	$1.5 \cdot 10^{15}$ $1.35 \cdot 10^{15} a)$
$1 \cdot 10^{15}$	87	62	$1.8 \cdot 10^{15}$
$2 \cdot 10^{15}$	74	62	$2.0 \cdot 10^{15}$
$5 \cdot 10^{15}$	42	53	$2.9 \cdot 10^{15}$

Table 3. Normalized additional net donor concentration, ΔN_D , and selenium neutral double donor concentration, Δn_T , in the epitaxial layer of the selenium-implanted transistors.

Sample Se dose (cm^{-2})	$\frac{\Delta N_D}{\Delta N_D(5 \cdot 10^{15})}$	$\frac{\Delta n_T}{\Delta n_T(5 \cdot 10^{15})}$
$5 \cdot 10^{15}$	1	1
$2 \cdot 10^{15}$	0.26	0.21
$1 \cdot 10^{15}$	0.17	0.13



- | | | | |
|----|-------------------|----|-----------------|
| 1. | BURIED LAYER | 5. | ISOLATION |
| 2. | ISOLATION IMPLANT | 6. | LOW DOPED BASE |
| 3. | EPITAXIAL LAYER | 7. | HIGH DOPED BASE |
| 4. | PLUG | 8. | EMITTER |

Fig.1 npn transistor structure used in the experiments.

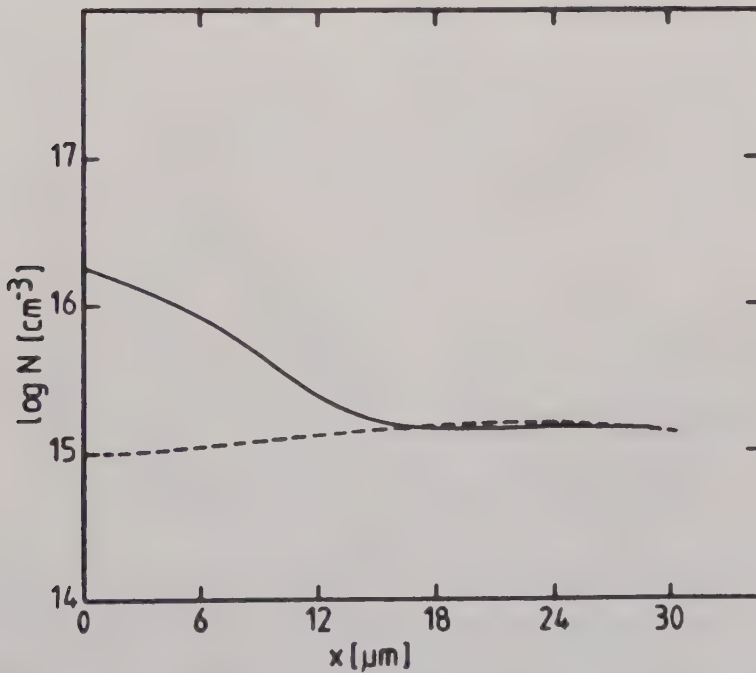


Fig.2 Charge carrier profile calculated from spreading resistance measurements for n-type monitor samples. Solid curve: selenium-implanted sample with a dose of $2 \times 10^{15} \text{ cm}^{-2}$, dashed curve: reference sample.

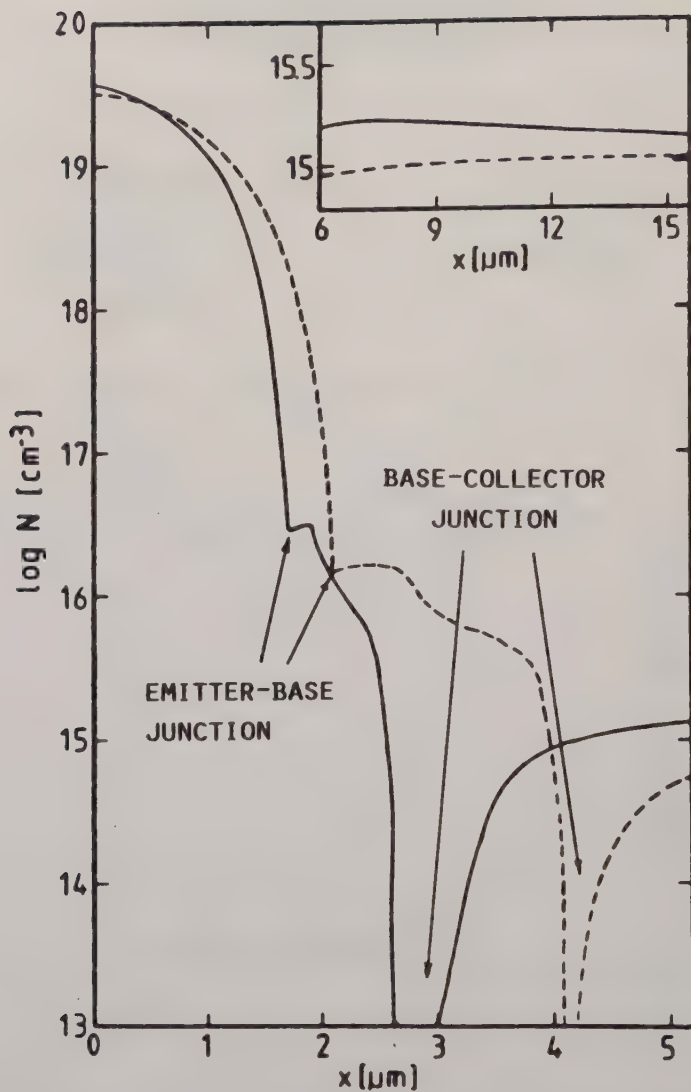


Fig.3 Charge carrier profile, calculated from spreading resistance measurements, for an npn monitor structure. Solid curve: selenium-implanted sample with a dose of $2 \cdot 10^{15} \text{ cm}^{-2}$, dashed curve: reference sample.

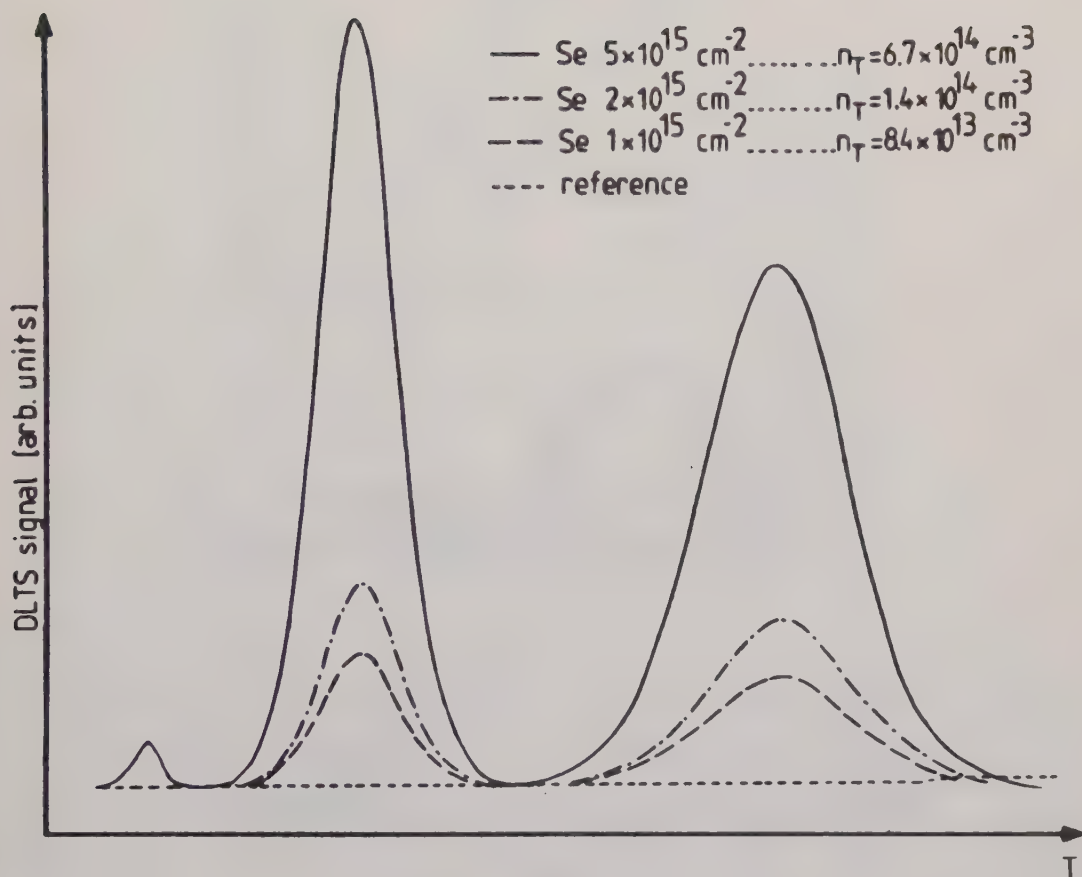


Fig.4 DLTS spectra obtained for collector-base diodes of the selenium-doped and reference transistors.

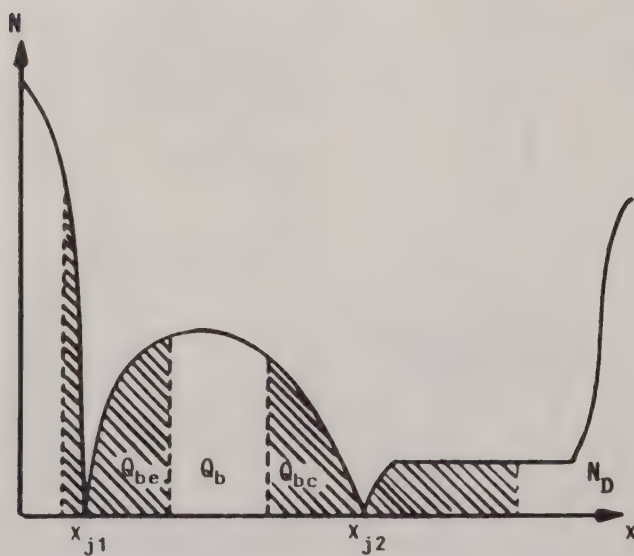


Fig.5 Doping profile for a standard epitaxial transistor showing the charges associated with their respective depletion regions as used in the proposed model.

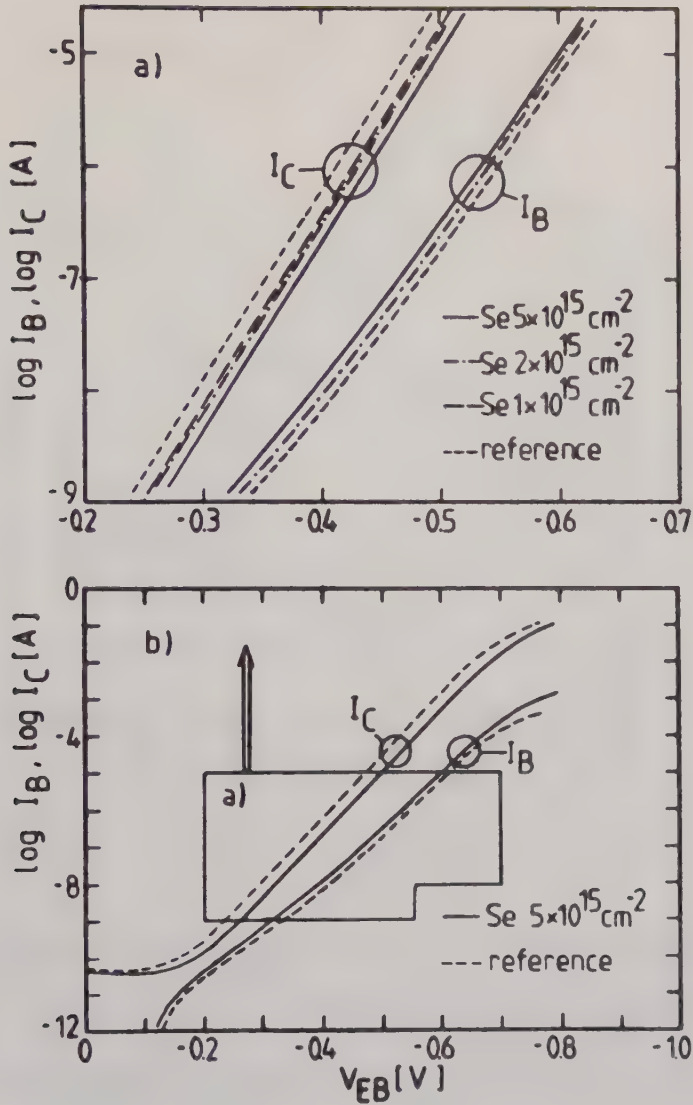


Fig.6 Gummel plot (collector current I_C and base current I_B as a function of emitter-base voltage V_{BE}) for for the npn transistors implanted with various selenium doses at $V_{CB} = 4\text{V}$. The base current, I_B , for the sample implanted with a selenium dose of $1 \times 10^{15} \text{ cm}^{-2}$ is only slightly smaller than for the sample implanted with a dose of $2 \times 10^{15} \text{ cm}^{-2}$.

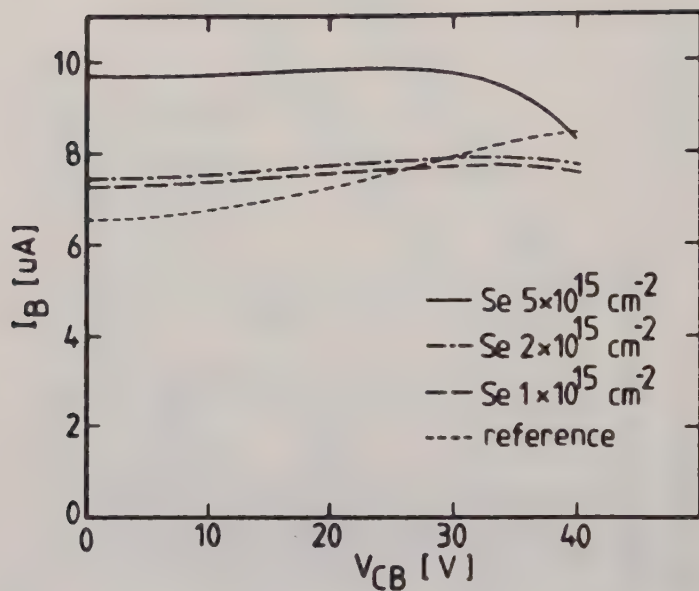


Fig.7 The base current of transistors implanted with various selenium doses at $V_{BE} = 0.6$ V. At the highest voltages the transistors are approaching the avalanche region, which is lowest for the transistor implanted with a selenium dose of $5 \times 10^{15} \text{ cm}^{-2}$.

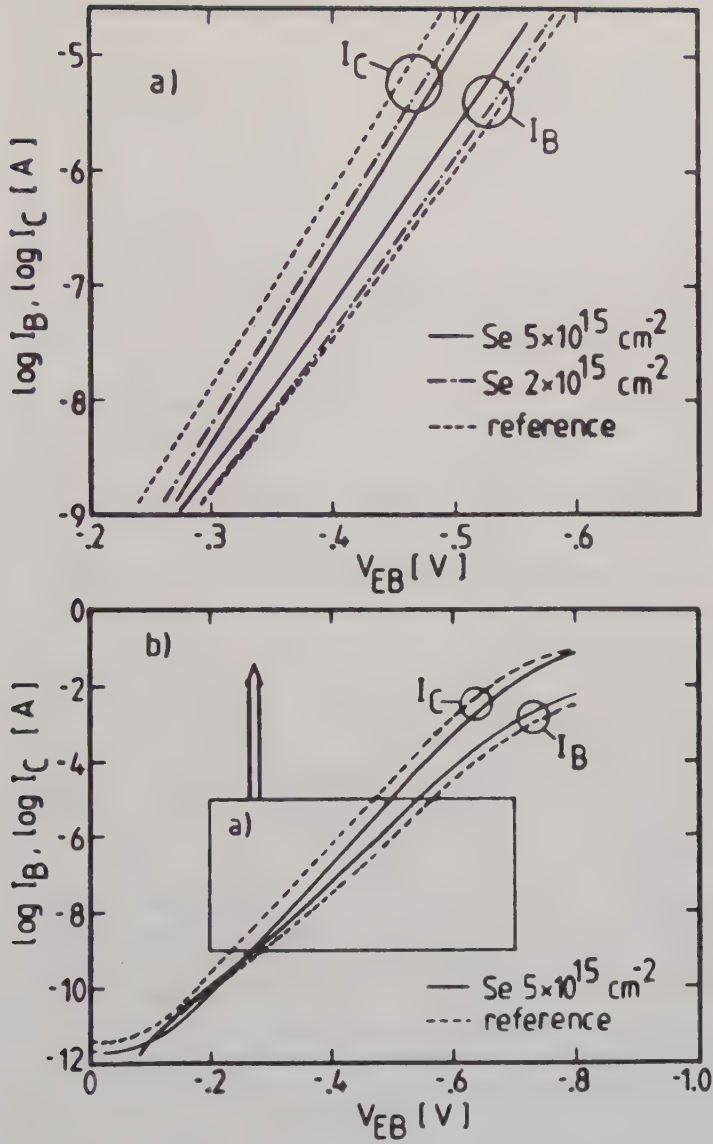


Fig.8 Gummel plot (collector current I_C and base current I_B as a function of emitter-base voltage V_{BE}) for inverse operating npn transistors implanted with various selenium doses at $V_{CB} = 0.5\text{V}$.

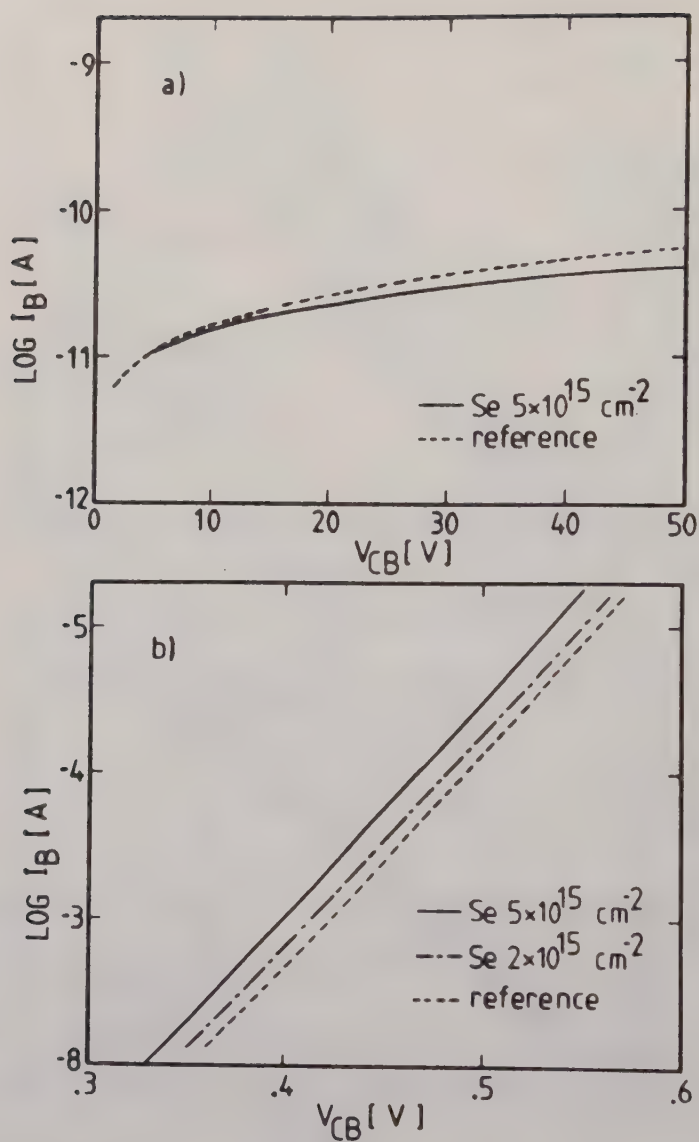


Fig.9 I-V characteristics of the selenium-implanted and reference collector-base diodes: a) reverse, b) forward. The reverse currents for the diodes with other selenium doses than those shown in the figure were close to the plotted values.

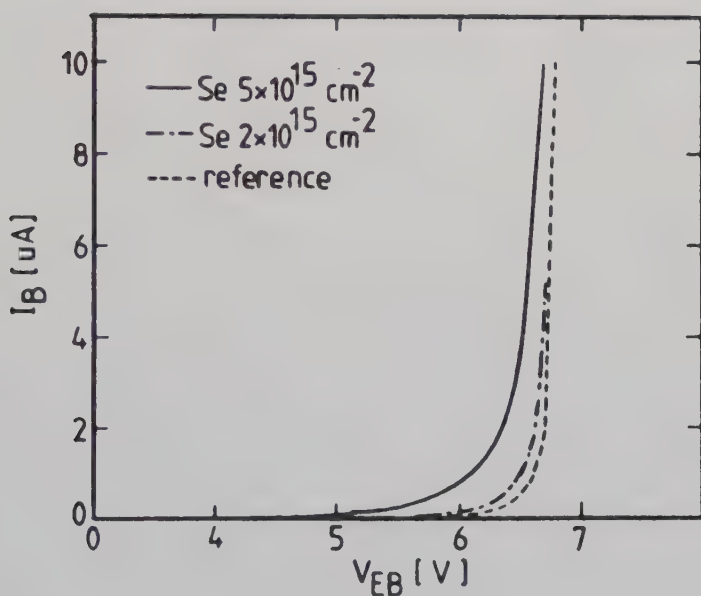


Fig.10 I-V reverse characteristics, showing breakdown voltage, of the emitter-base diodes of npn transistors implanted with various selenium doses. The breakdown voltage, BV_{EB0} , for the transistor implanted with a dose of $1 \times 10^{15} \text{ cm}^{-2}$ (not shown in figure) is only slightly higher than the breakdown voltage for the transistor implanted with a dose of $2 \times 10^{15} \text{ cm}^{-2}$.

**ANOMALOUS PHOSPHORUS AND BORON DIFFUSION IN SELENIUM-IMPLANTED
NPN SILICON TRANSISTORS.**

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Abstract

Impurity distributions in Se-implanted Si double-diffused npn transistors have been studied using SIMS, SRP and DLTS techniques. Transistors implanted with Se doses of $1-5 \times 10^{15} \text{ cm}^{-2}$ showed emitter junction depths of about $1.5 \text{ } \mu\text{m}$, which was $0.5 \text{ } \mu\text{m}$ shallower than the emitter junction depth of a reference transistor. The base junction depths also became shallower in the Se-doped devices. This is interpreted as being the result of anomalous diffusion effects and compensation of the boron acceptors in the base by Se donors.

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ANOMALOUS PHOSPHORUS AND BORON DIFFUSION IN SELENIUM-IMPLANTED NPN SILICON TRANSISTORS.

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I INTRODUCTION

Optical and electronic properties of Se in Si have been investigated through the years. Se-doped Si has found some application in IR-detectors [1]. Se in Si introduces a number of donor levels. Recently, it has been shown that the two-electron level of an isolated, substitutional, Se double donor in Si has electron- and hole-capture cross-sections of the same order of magnitude, $\sigma_n = \sigma_p = 10^{-16} \text{ cm}^2$ [2,3]. This level, with a Gibbs free energy of $E_C - 0.30 \text{ eV}$, may be involved in the recombination process (depending on the position of the Fermi level). The hole-capture cross-section to the one-electron level, with a Gibbs free energy of $E_C - 0.57 \text{ eV}$, is of the order of 10^{-23} cm^2 [2] and the electron-capture cross-section is larger than 10^{-14} cm^2 [3]. In practice, this implies that this level is exclusively an electron trap.

To evaluate the properties of Se-doped Si devices, some npn transistors were produced. The evaluation of the transistor properties showed that both the base and the emitter became shallower than in reference transistors [4]. Electrical measurements indicated an increased acceptor concentration in the base at the emitter-base junction. In addition, material investigations were performed in order to gain an understanding of the underlying physical phenomena.

This paper is part of a larger effort to evaluate the role of Se in silicon devices. Spreading Resistance Probe and Secondary Ion Mass Spectroscopy techniques were employed to investigate P and B diffusions in Se-implanted npn transistors. Possible explanations of the observed phenomena are discussed.

II EXPERIMENTAL DETAILS

a. SAMPLE PREPARATION

Ion implantation was used as a source of Se to assure selective doping. The transistor preparation procedure after base diffusion is shown in Fig.1. The previous steps were performed as for a standard bipolar, high-voltage, integrated circuit (IC) process and are described elsewhere [4]. Three different Se doses: 1×10^{15} , 2×10^{15} and $5 \times 10^{15} \text{ cm}^{-2}$, were implanted at 50 keV in emitter openings, each dose on a quadrant of a wafer. One quadrant was spared for reference transistors. After implantation, an approximately 2- μm -deep layer was formed by phosphorus deposition at 920°C for 20 minutes and diffusion in an oxidizing atmosphere at 1010°C for 50 minutes. A 200 nm CVD SiO_2 layer was deposited and annealed for 40 minutes at 1000°C. The aluminium contacts were sputtered and alloyed for 30 minutes at 450°C in an N_2 atmosphere. The reason for implanting selenium exclusively in the emitter area was to avoid any implantation damage at the base surface. Such damage would have affected the characteristics of the investigated devices in an uncontrolled manner. In the following, these devices will be referred to as transistors.

To check a hypothesis that it was the phosphorus deposition into the ion-implantation-damaged surface which was responsible for the

shallower emitter, Se was implanted after emitter diffusion. This was done with a dose of $2 \times 10^{15} \text{ cm}^{-2}$ at 100 keV on part of a Si wafer prepared as above, but this time without any device structure. The non-implanted area was used later as a reference for the implanted samples. The selenium implantation was followed by annealing for 10 minutes in an $\text{N}_2 + \text{O}_2$ atmosphere and 1 hour in an O_2 atmosphere at 1000°C . In the following, the samples made in this way will be referred to as npn structures.

b. ANALYSIS METHODS

The samples were analysed using the following methods:

1. Junction depth, x_j , measurements on the transistors.

Samples were angle-lapped with Al_2O_3 powder and the angle measured. pn junctions were revealed by staining with a solution of CuSO_4 and HF in water and measured using a microscope.

2. Concentration of the isolated Se double donors in the transistors.

Deep-Level Transient Spectroscopy (DLTS) [5] measurements were performed on collector-base diodes of the transistors and the concentration of the Se double donors computed [4] (see footnote*).

*(Footnote:) Only part of the Se electrical activity in Si can be measured in this way since Se gives rise to other donor defects than isolated double donors [6.7].

3. Free carrier concentration profiles in the npn structures.

Samples were angle-lapped with Al_2O_3 powder, the angle measured and the electrical resistivity measured as a function of the depth using a Spreading Resistance Probe (SRP) method. The concentration profile of the free carriers was then computed from the SRP data.

4. Chemical concentration profile in the npn structures.

Samples were studied using Secondary Ion Mass Spectroscopy (SIMS).

In addition, electrical measurements were performed on the transistors, but these are beyond the scope of this paper. The results are published elsewhere [4].

III EXPERIMENTAL RESULTS

a. NPN TRANSISTORS.

The micrographs of the angle-lapped and stained transistors are shown in Fig.2. The emitter depth topology is not real but a result of the emitter design, with the emitter stripes in a grid, combined with the angle-lapping procedure. The base depth of the transistor implanted with Se varies, with the shallower base under the emitter stripes. The results of junction depth measurements are presented in Table 1. It is apparent that the emitter and base junctions are shallower in Se-implanted transistors than in the reference transistor. However, no significant differences could be measured for Se doses of $1 \times 10^{15} \text{ cm}^{-2}$ and $2 \times 10^{15} \text{ cm}^{-2}$.

The DLTS measurements were performed on the collector-base diodes of the transistors [4] and the spectra are shown in Fig.3. The

concentrations of the Se double donors were calculated and are presented in Table 1.

b. NPN STRUCTURES.

The depth distributions of the free charge carriers in the npn structures, computed from the SRP data, are shown in Fig. 4. Also in this case both emitter and base junctions are shallower in the Se-implanted sample than in its reference. The emitter is shallower by about 0.4 μm .

An additional piece of information is gained from SIMS measurements. Fig. 5 shows the distribution of P and B in the npn structures and Fig. 6 the distribution of Se.

The Se concentration profile is very deep in accordance with the known data on its relatively high diffusivity [7]. The Se concentration distribution could not be quantified because of the lack of Si reference samples with known Se concentrations. However, there is an upper concentration limit of about 10^{16} cm^{-3} given by the solubility of Se in Si at the annealing temperature of 1000°C [7].

The boron distribution in Se-implanted npn structures differs from the reference. The concentration is slightly higher and, while in the reference the depth distribution is almost logarithmic, there is a bump in the distribution at a depth of about 1.5 μm in the Se-doped npn structure.

The phosphorus profile has undergone a much more significant change than the boron profile in the Se-doped sample. The diffusion depth is shallower by about 0.5 μm compared with the reference sample. The SIMS

profiles are very similar to the SRP profiles. An additional test showed that during the same annealing process as the one following the Se implantation, the phosphorus emitter diffused about 0.5 μm into the Se-free reference p-type wafer.

The differences in diffusion depths of Se-doped and reference npn structures are accounted for by differences occurring during the annealing process. The results imply that the phosphorus diffusion during the annealing process was practically inhibited by Se implantation.

IV DISCUSSION

From the above results, it is obvious that Se implantation, followed by diffusion, affects both chemical and electrical impurity distributions in Si npn transistors.

Se is a fast diffusant in Si [7] and gives rise to several donor levels in the energy band gap [6]. An expected result of Se diffusion into the npn transistor structures is a compensation of B acceptors in the base. This reveals itself as a shallower SRP profile of the base, while the depth of the SIMS profile is not affected. The difference between the net acceptor concentration, measured with SRP, and total acceptor concentration measured using SIMS, is given by Se donors. Fig. 2 demonstrates this very clearly. The base is shallower under emitter stripes, where Se was ion implanted. The shallowest base is found in the transistors implanted with the highest Se dose of $5 \times 10^{15} \text{ cm}^{-2}$. DLTS measurements showed the highest concentration of the Se double donors in these transistors.

The cause of the change in P and B distributions in Se-doped samples is less clear. The results of SIMS measurements showed that P diffusion was retarded while the B diffusion was enhanced.

An explanation of the emitter diffusion retardation could be disorder-induced stress caused by ion damage during implantation. Such an effect was demonstrated a few years ago for the ion damage caused by the implanted P impurity itself [8] and by ion damage due to irradiation by neutral species (Ne^+) [9]. In the last case, the diffusion was shown to be retarded with increasing Ne^+ dose, up to a dose of 10^{15} cm^{-2} , followed by saturation. Taking into account the larger mass of Se atoms, it is likely that for Se doses of 10^{15} cm^{-2} and greater, the diffusion retardation of phosphorus in the transistors is already in the saturation region. This assumption is supported by the fact that all Se-implanted transistors have almost the same emitter depth, significantly different from the reference transistors.

Also, it does not seem to matter at what stage in the process the Se implantation takes place. Se was implanted both before and after emitter diffusion (followed by annealing) and in both cases the result was a significantly shallower emitter.

Implantation-induced strain has been shown to retard even B diffusion [9]. Apparently this is not the case in our experiment as can be seen in Fig. 5. The B diffusion is instead somewhat enhanced.

An explanation of the anomalous B profile in Se-implanted samples could be cooperative diffusion effects. In general it is accepted that diffusivity enhancement of the base dopant results from a

supersaturation of intrinsic point defects. This supersaturation is related to a high surface concentration of phosphorus. In the Se-implanted transistors, on the other hand, there are some further complications. Thus, the solid solubility of Se in Si (about 10^{16} cm^{-3}) is exceeded because of the rather high implanted doses ($>10^{15} \text{ cm}^{-2}$) which could cause a further increase in the defect generation. Furthermore, the simultaneous presence of Se, P and B could lead to additional cooperative effects during the diffusion.

The mechanisms of Se diffusion in Si are little known. Se is a fast diffusant, however not as fast as impurities in markedly interstitial solutions, such as Au or Fe. Back-scattering experiments on Si samples implanted with Se [10] have indicated a substitutional fraction of 30%. Se may thus affect the concentrations of both vacancies and interstitials during the diffusion process.

In silicon, a multiple-charge-state vacancy model is assumed valid for diffusion mechanisms even if the possibility of diffusion via interstitials [11] has also been suggested. Thus, it is likely that Se diffusion in Si affects even the diffusivities of other impurities such as B and P.

V CONCLUSIONS

Se implantation and subsequent high-temperature annealing affect the diffusivities of P and B in Si npn transistors. The P diffusion is retarded while B diffusion is enhanced in a way similar to the emitter-push effect. The disorder-induced stress caused by ion damage during ion implantation and the cooperative diffusion effects due to Se impurity diffusion are assumed to be responsible for the anomalies. However, no models can be proposed because of the lack of knowledge

regarding Se diffusion mechanisms in Si. Further investigations are indispensable if we are to understand the basic processes of Se diffusion in Si.

Acknowledgments

I would like to thank Dr U. Smith and Dr P-O Larsson for valuable discussions and Thorbjörn Pihl from the Microwave Institute in Stockholm for performing the ion implantations. The valuable assistance of Prof. H.G. Grimmeiss during the course of this work is gratefully acknowledged.

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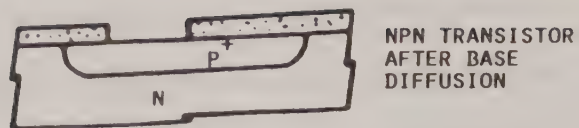
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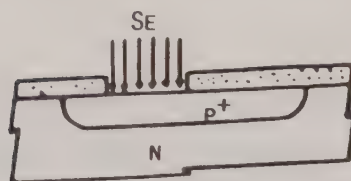
Table 1.

Junction depths of the angle-lapped and stained npn transistors implanted with various Se doses, and concentrations of Se neutral double donors, n_T , at collector-base junctions of the transistors calculated from DLTS measurements.

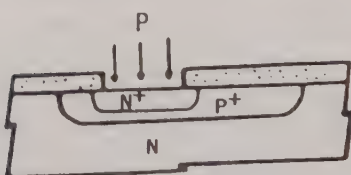
Se dose (cm^{-2})	Ref.	$1 \cdot 10^{15}$	$2 \cdot 10^{15}$	$5 \cdot 10^{15}$
Emitter depth (μm)	2.0	1.6	1.6	1.5
Base depth (μm)	3.4	3.2	3.2	2.9
n_T (cm^{-3})	-	$8 \cdot 10^{13}$	$1.5 \cdot 10^{14}$	$7 \cdot 10^{14}$



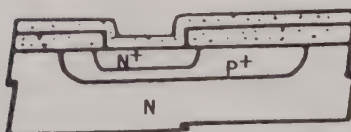
NPN TRANSISTOR
AFTER BASE
DIFFUSION



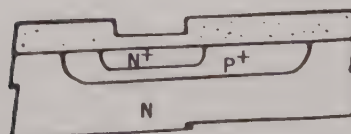
SELENIUM
IMPLANTATION



PHOSPHORUS
PREDEPOSITION
AND DIFFUSION



CVD SiO_2
DEPOSITION
AT 420°C



ANNEALING
AT 1000°C

CONTACT HOLES AND
METALIZATION

Fig. 1 Preparation procedure for npn transistors.

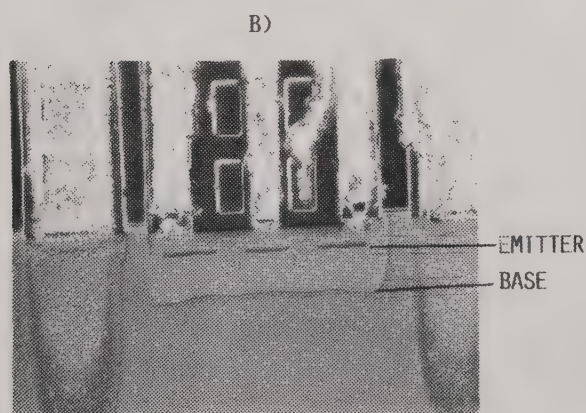
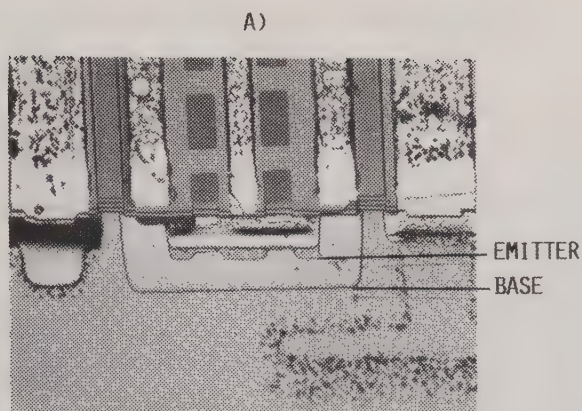


Fig. 2 Micrographs of angle-lapped and stained transistors:
 a) reference b) Se-implanted with a dose of $5 \cdot 10^{15} \text{ cm}^{-2}$. The irregular collector-base junction depth is a result of selective Se ion implantation in the emitter stripes and following compensation of the base acceptors by Se donors only under the emitter stripes.

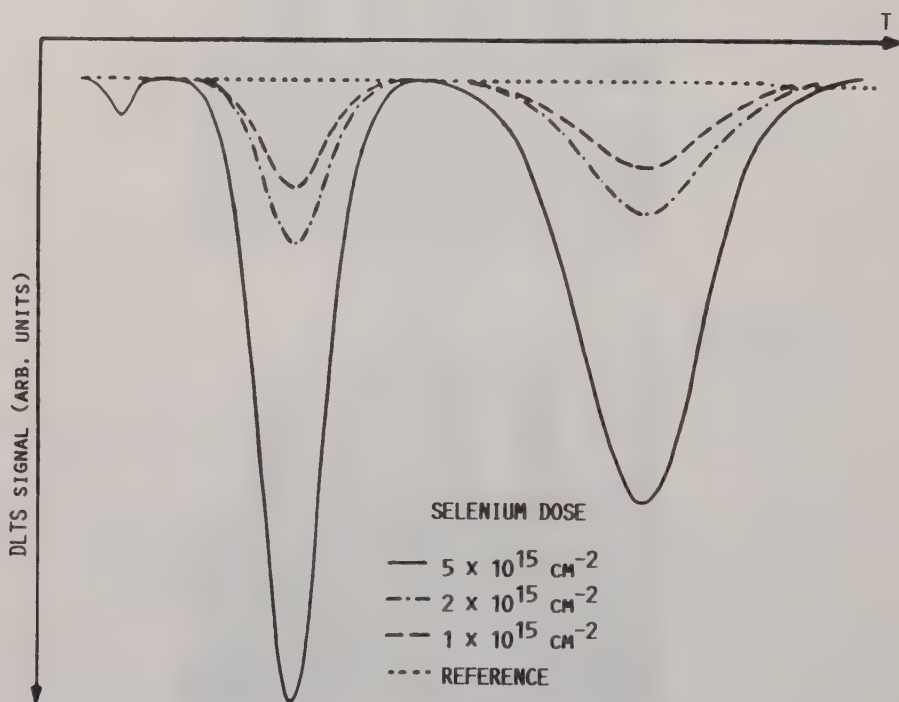


Fig. 3 DLTS spectra of collector-base diodes of the npn transistors implanted with various Se doses.

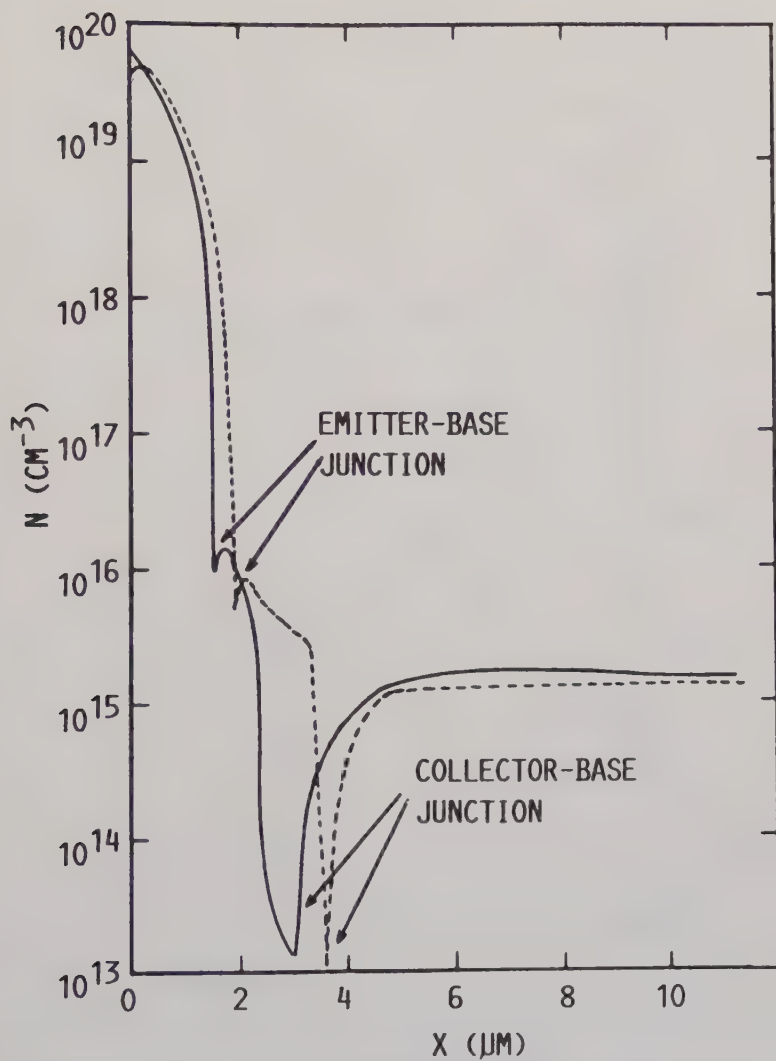


Fig. 4 Free charge carrier profile, computed from SRP data, for the npn structures. Solid curve: Se-implanted sample with a dose of $2 \times 10^{15} \text{ cm}^{-2}$, dashed curve: reference sample.

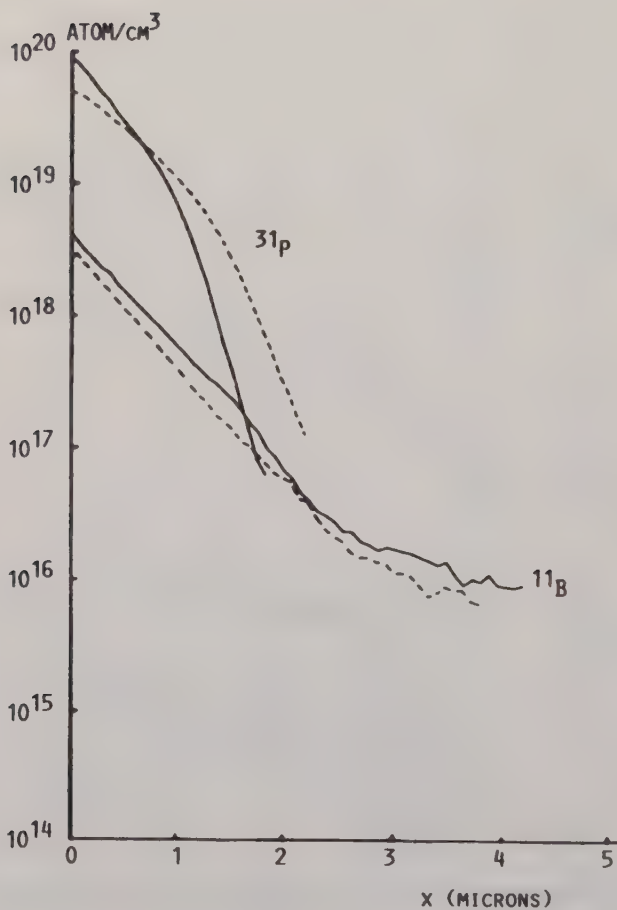


Fig. 5 SIMS profile of P and B distributions in npn structures. Solid curve: Se-implanted sample with a dose of $2 \times 10^{15} \text{ cm}^{-2}$, dashed curve: reference sample.

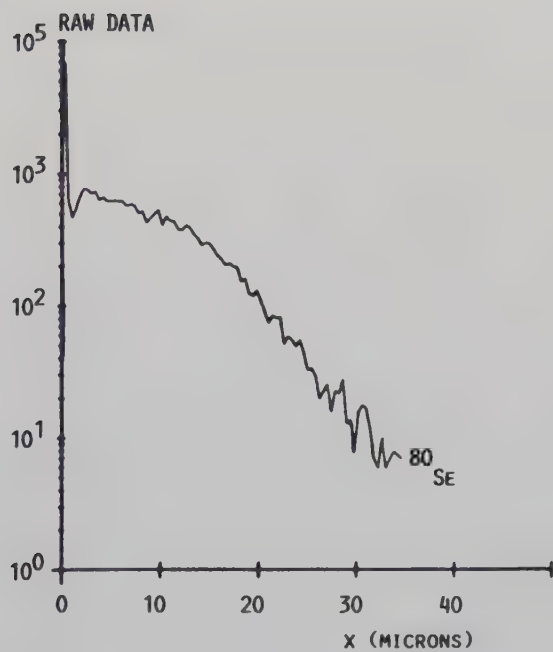


Fig. 6 SIMS profile of Se in npn structure, raw data. The Se concentration could not be quantified due to the lack of a Se-doped Si calibration reference.

V

SWITCHING PROPERTIES OF SELENIUM-DOPED SILICON NPN TRANSISTORS

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Abstract. Pulse measurements, performed on selenium-doped transistors, showed a decreased turn-off storage time with increasing implanted selenium dose. The shortest turn-off time, for a device implanted with a Se dose of $5 \cdot 10^{15} \text{ cm}^{-2}$, was only one fifth of the turn-off time for a reference transistor. The reasons for this decrease are discussed in terms of lower current gains for the transistors and a shorter lifetime for the excess charge carriers in the epitaxial collector.

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SWITCHING PROPERTIES OF SELENIUM-DOPED SILICON NPN TRANSISTORS

A. Litwin[†], Department of Solid State Physics, University of Lund, Box 118, S-221 00 Lund, Sweden.

I. INTRODUCTION

Deep-level impurities have a profound effect on semiconductor device performance. In silicon devices the generation-recombination properties are determined by deep-level defects. These properties do not only affect the steady-state characteristics but also the switching properties by controlling the lifetime of the excess charge carriers. Gold, platinum and lately electron irradiation have been employed to reduce the lifetime in silicon devices. However, none of these methods is suitable for selective application, for use in integrated circuits. Recent research on the electronic properties of Se in Si has shown that the shallowest of the levels created by the isolated, substitutional, Se double donor acts as a recombination centre in n-type Si [1-3]. Since Se is used as a donor dopant for GaAs, there is an already developed and easily accessible technique for ion implantation. This method can also be applied to dope Si devices with Se.

The purpose of this paper is to report on the results of an investigation of the switching properties of Se-doped Si npn transistors.

II. EXPERIMENTAL DETAILS

The studied transistors were parts of high-voltage, bipolar, integrated circuits. The manufacturing procedure is described elsewhere [4]. Se ions were selectively implanted in the emitter openings using a photoresist mask. Three different doses were applied at 50 keV, viz. 1, 2 and $5 \cdot 10^{15} \text{ cm}^{-2}$. Se was then diffused together with the phosphorus emitter.

The concentration of Se double donors was measured using the Deep-Level Transient Spectroscopy (DLTS) technique [5]. This was performed at the collector-base junction of the transistors and gave the concentration of the Se double donors in the epitaxial collector under the emitter areas. The results are summarized in Table 1.

The electric parameter measurements were performed using a Hewlett-Packard 4145A Semiconductor Parameter Analyser, a Hewlett-Packard 3312 A Function Generator and a Tektronix 7704 A oscilloscope.

III. RESULTS

The turn-off delay times of the transistors were studied using the set-up shown in Fig.1. The results are presented in Table 1. Photographs of the input and output pulses for a Se-doped and a reference transistor are shown in Fig. 2.

Since the forward and reverse common-emitter current gains, h_{FE} , are among the determining factors for the turn-off storage time, they were measured, and are plotted in Fig. 3. From the h_{FE} values the common-base current gain, α , can be calculated using the expression

$\alpha = h_{FE}/(h_{FE} + 1)$. The results of other various steady-state measurements are published elsewhere [4].

IV. DISCUSSION

Transistor switching properties have been studied in theory and very accurate models have been proposed [6,7]. An elegant presentation of the models is made by Phillips [8].

A qualitative treatment can be used for the storage time for a transistor, using the expression [8]

$$t_s = \tau_s \ln \frac{I_{B1} - I_{B2}}{I_C/h_{FE} - I_{B2}} \quad (1)$$

with the storage time constant

$$\tau_s = \frac{\tau_E + \alpha \alpha_R \tau_{ER}}{1 - \alpha \alpha_R} + \frac{\alpha(1 - \alpha_R) \tau_{CS}}{1 - \alpha \alpha_R} \quad (2)$$

The notation is the same as in Ref. [8]. Here τ_E and τ_{CS} are emitter and collector time constants, respectively, α is the common-base current gain and the index R denotes reverse operation of the transistor.

For a planar transistor with a graded base the following approximations can be used: $\tau_E = 0.6/\omega_b$, $\tau_{ER} = 2.4/\omega_b$ and $\tau_{CS} = \tau_{nc}$, where ω_b is the base-cutoff frequency and τ_{nc} the effective collector lifetime. Thus, Eqn. 2 can be rewritten.

$$\tau_S = \frac{1}{\omega_b} \left(\frac{0.6 + 2.4\alpha\alpha_R}{1 - \alpha\alpha_R} \right) + \tau_{nc} \frac{\alpha(1 - \alpha_R)}{1 - \alpha\alpha_R} \quad (3)$$

The transistors in this experiment have $\alpha \approx 1$ and inverse α_R which cannot be neglected since even for rather low currents it is larger than 0.5. Thus, Eqn. 1 is simplified to:

$$t_S = \left(\frac{1}{\omega_b} \frac{0.6 + 2.4\alpha\alpha_R}{1 - \alpha\alpha_R} + \tau_{nc} \right) \ln \frac{I_{B1} - I_{B2}}{I_C/h_{FE} - I_{B2}} \quad (4)$$

The short storage time is accomplished by two means (assuming unchanged base-cutoff frequency ω_b): low current gain and short collector lifetime. Both of these effects occur in Se-doped transistors. Forward and reverse current gains decrease with increasing Se dose, as shown in Fig. 3.

τ_{nc} is an effective collector lifetime and depends on a number of design factors. The lifetime term, depending on the recombination in a Se-doped n-type epitaxial layer, is inversely proportional to the Se double donor concentration N_{TT} (cm^{-3}) and is given by the expression [3]

$$\tau^{-1} = 10^{-9} N_{TT} \text{ (s}^{-1}\text{)}$$

The delay time decreases in the Se-implanted transistors and thus follows qualitatively Eqn. 4. Since some of the parameters in Eqn. 4 are extremely difficult to extract from existing devices, at the present time no comparisons can be made between the calculated and measured values of the delay time.

V. CONCLUSIONS

The switching properties of Si npn transistors are improved by Se-doping even if other undesirable effects occur e.g. the decrease in forward current gain. However, some of these negative effects could be circumvented by an alternative transistor design. Since Se can be implanted selectively, it is possible to dope the area outside the emitter region and avoid the decreased forward current-gain, mentioned above.

Acknowledgments

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Table 1. Storage time, t_s , for transistors implanted with various Se doses, and concentrations of Se neutral double donors, n_T , at the collector-base junction of the transistors, calculated from DLTS measurements.

t_s (μs)			
Sample	$I_C=10mA$	$I_C=10mA$	n_T
Se dose (cm^{-2})	$V_{BE}=0.9V$	$V_{BE}=1.6V$	(cm^{-3})
Reference	0.57	1.35	-
$1 \cdot 10^{15}$	0.40	1.20	$8 \cdot 10^{13}$
$2 \cdot 10^{15}$	0.33	1.10	$1.5 \cdot 10^{14}$
$5 \cdot 10^{15}$	0.11	0.75	$7 \cdot 10^{14}$

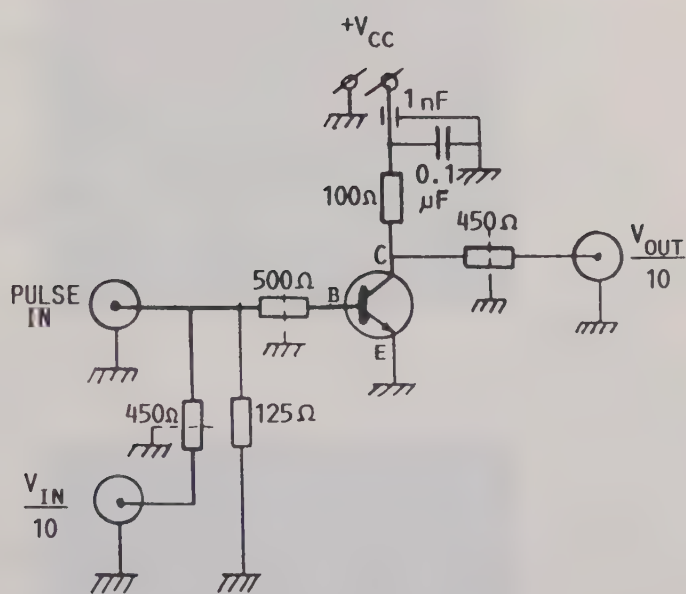


Fig. 1 The 50-ohm-adapted set-up used for pulse measurements on transistors.

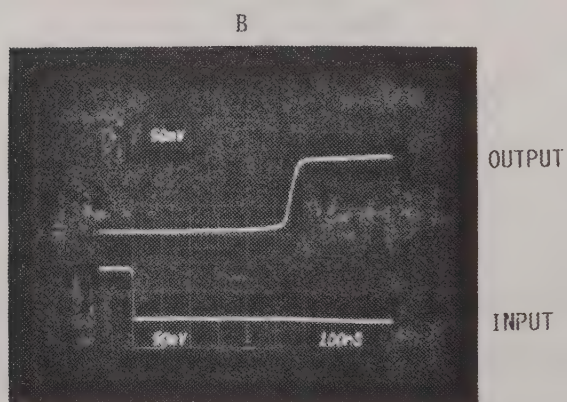
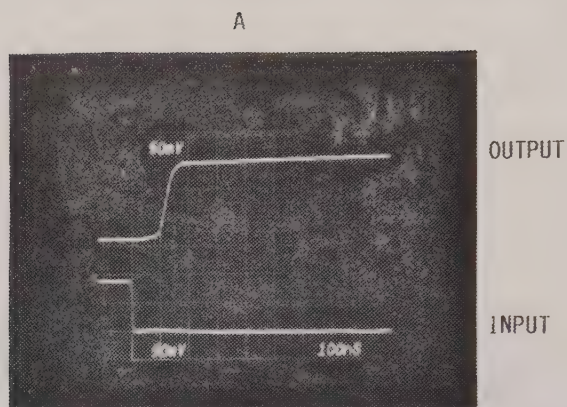


Fig. 2 The input and output pulses showing the turn-off delay time for: A) a transistor implanted with a Se dose of $1 \cdot 10^{15} \text{ cm}^{-2}$ and B) a reference transistor.

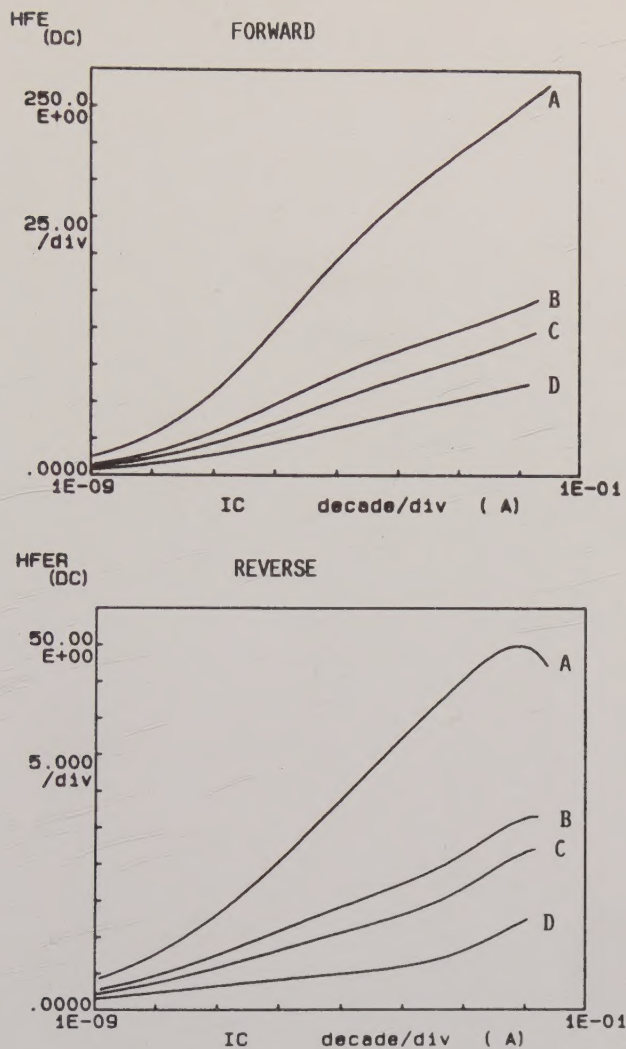


Fig. 3 Forward and reverse common-emitter current gains, h_{FE} , for transistors implanted with Se doses of:
 A) reference, B) $1 \cdot 10^{15} \text{ cm}^{-2}$, C) $2 \cdot 10^{15} \text{ cm}^{-2}$,
 D) $5 \cdot 10^{15} \text{ cm}^{-2}$.

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